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Kirsti Kalevi

Two interlaboratory comparisons of analysis of chlorophenols in soil samples

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FOREWORD

In the beginning of 1990's investigations and remediations of old saw mills polluted with the chlorophenol preservative, Ky 5, were initiated. Analysis of chlorophenols as well as any other contaminant in soil, was very variable. There was almost as many analysing methods as analysing laboratories. The Finnish Environment Institute compared three different methods and this gave such results that an idea raised to arrange a collaborative ringtest to find out the situation of analysing chlorophenols in soil samples. The ringtest was arranged in 1995 and the purpose was to compare the results of methods used for analysing chlorophenols in Finland.

In 1995 a Nordtest project "Nordic Guidelines for Chemical Analysis of Contaminated Soil Samples" was carried out. The aim of this project was to get recommendations for analysing the most common contaminants in soil. This was followed by the project "Validation and ringtesting of chemical analyses for contaminated soil" in 1996. Each participating country arranged one Nordic interlaboratory test. The Finnish Environment Institute arranged a test concerning chlorophenols in contaminated soil. Each participating laboratory had to analyse samples with the recommended method but they could also analyse with their own method.

PART I

Comparing methods for analysis of chlorophenols in soil samples by a ringtest in 1995

CONTENTS

1 INTRODUCTION

The analysis of chemical contaminants in soil samples and the standardization of extraction methods used are in rapid development. Only few standards exists and usually there is no commonly used analysis procedure. The behaviour of compounds in soil differs a lot from their behaviour in water and chlorophenols do not cause an exception. With investigation of contaminated soil sites the demand for analytics of chlorophenols has increased. The abundance of known methods and the variability of results has raised a question about the reliability of chlorophenol analyses. This is the background for arranging this collaborative ringtest.

The ringtest was arranged in spring 1995 and the aim was to study differencies of methods in use. Finally thirteen laboratories were participating and they analyzed samples using their own methods.

2 PERFORMANCE OF RINGTEST

2.1 Participating laboratories

Announcement to participate in the ringtest came from fourteen laboratories and results were finally recieved from thirteen laboratories of which eleven were from Finland and two from Sweden (appendix 1). Laboratories were national research institutes and municipal or private laboratories. Three laboratories have analyzed the samples with several methods for comparation.

2.2 Samples to be compared

For analysing chlorophenols all the laboratories got three authentic soil samples from a sawmill. When preparing samples the soils was sieved three times through an 8 mm sieve. The concentration in sample 2 was remarkably high and it contained quite a lot of saw dust. These two things were criticized by several of the participating laboratories, but we wanted the samples to be as authentic as possible because real samples often are like this.

Samples 1 and 3 were the same sample but sample 3 had been spiked with known concentrations (Table 1) of 2,4,6-trichlorophenol, 3,4,5-trichlorophenol, 2,3,4,6-tetrachlorophenol and pentachlorophenol.

Table 1:

CONCENTRATIONS OF COMPOUNDS SPIKED IN SAMPLE 1:				
Compound	mg/100ml	mg/4,002 kg wet	mg/kg wet	mg/kg dry
246-TCP	5.6	5.6	1.399	1.824
345-TCP	4.6	4.6	1.149	1.499
2346-TeCP	48	48	11.994	15.638
PCP	8	8	1.999	2.606

Every laboratory received 200 grams of each sample in the same kind of jars.

2.3 Analytical methods

Each laboratory analyzed the samples with their own method, which they were asked to describe thoroughly (appendix 3). The number of chlorophenols analyzed by the laboratories was quite variable. Some analyzed only the components of the commercial KY-5 product, the most commonly used wood preservative in Finland, and the others almost all possible chlorophenols.

2.3.1 Extraction

Several different extraction procedures were used, but they could be grouped into five main groups. Namely extraction with base, acidic acetone, acetone-hexane, carbonate and solvent. Basic extraction had been done with sodium hydroxide and with mixture of potassium hydroxide and methanol. Solvent extractions had been done with toluene, acetonitrile, acidic ether and solvent mixture containing hexane, acetone, diethyether and petroleumether.

Extraction equipments used were Soxhlet apparatus, ultrasonic bath, ultrasonic shaker, ordinary shaker or even mixing with glas stick. Time of extraction varied from 5 minutes to even 48 hours.

2.3.2 Derivatization

Almost all laboratories had used acetylation with acetic anhydride to produce derivatives. The amounts of reagents varied in different methods but in almost every case carbonate had been the buffer.

2.3.3 Analyzing and calculating the results

One laboratory used liquid chromatography and all other laboratories used gaschromatography for the analysis. The detector mostly used was ECD and in some laboratories used a mass spectrometer.

The results had been calculated with computer programs connected to the gas chromatographs or by separate calculation programs.

3 RESULTS

3.1 Measured concentrations and their variation

The averages of all compounds detected for each laboratory were calculatedand investigated further. In table 2 the averages, standard deviations and relative standard deviations for three most commonly analysed chlorophenol compounds are presented. Calculations were done both based on all reported results and based on results excluding outliers. Outliers were excluded by calculating value |z| , that is

$$|z| = (x' - x) / s,$$

where x' = average result from one laboratory
x = mean of all results
s = standard deviation of all results

The result was an outlier if $|z| > 2$.

Table 2. Measured chlorophenol concentrations of Ky 5-components in samples 1, 2 and 3.

Chloro-phenol	Sample	N, all results	Mean, all results	Stan-dard deviati-on	CV_r(%), all results	N, exclud-ing out-liers	Mean, exclud-ing out-liers	Stan-dard devia-tion	CV_r(%), exclud-ing out-liers
246-TCP	Sample 1	15	0.34	0.36	107.2	14	0.268	0.275	102.5
	Sample 2	13	9.37	9.06	96.7	12	6.94	3.53	50.9
	Sample 3	14	0.41	0.37	92.3	13	0.333	0.283	84.9
2346-TeCP	Sample 1	15	5.56	4.81	86.5	14	4.70	3,86	82.1
	Sample 2	15	388	441	113.7	13	225	129	57.6
	Sample 3	15	17.0	24.4	143.7	14	11.2	10.9	97.2
PCP	Sample 1	15	3.25	2.44	75.3	14	2.804	1.95	69.4
	Sample 2	15	2962	2440	82.4	14	2336	1272	54.5
	Sample 3	15	61.1	173	283.5	14	15.6	30.9	198.5

N = number of laboratories included in the interlaboratory test
CV_r(%) = repeatability variation coefficient

The deviation between results is quite large. Partly this is due to the fact that some laboratories tested new methods and their results differs quite a lot from other results.

In appendix 3 all the results are presented in a summary table and in appendix 4 some of the results are presented as line diagrams.

3.2 Influence of internal standard

The internal standard used by the partisipating laboratories was either 2,3,6-trichlorophenol or 2,4,6-tribromophenol in almost every case. Some laboratories used also 2,4-

dichlorophenol and 2,6-dichlorophenol simultaneously with the previous compounds. One laboratory used radioactive chlorophenols as internal standards.

In table 3 are compared methods, in which 2,3,6-trichlorophenol was used as internal standard, with those methods in which bromophenols were used. Because all laboratories had analyzed 2,4,6-trichlorophenol, 2,3,4,6-tetrachlorophenol and pentachlorophenol we used these as examples.

Table 3. Comparing of different internal standards

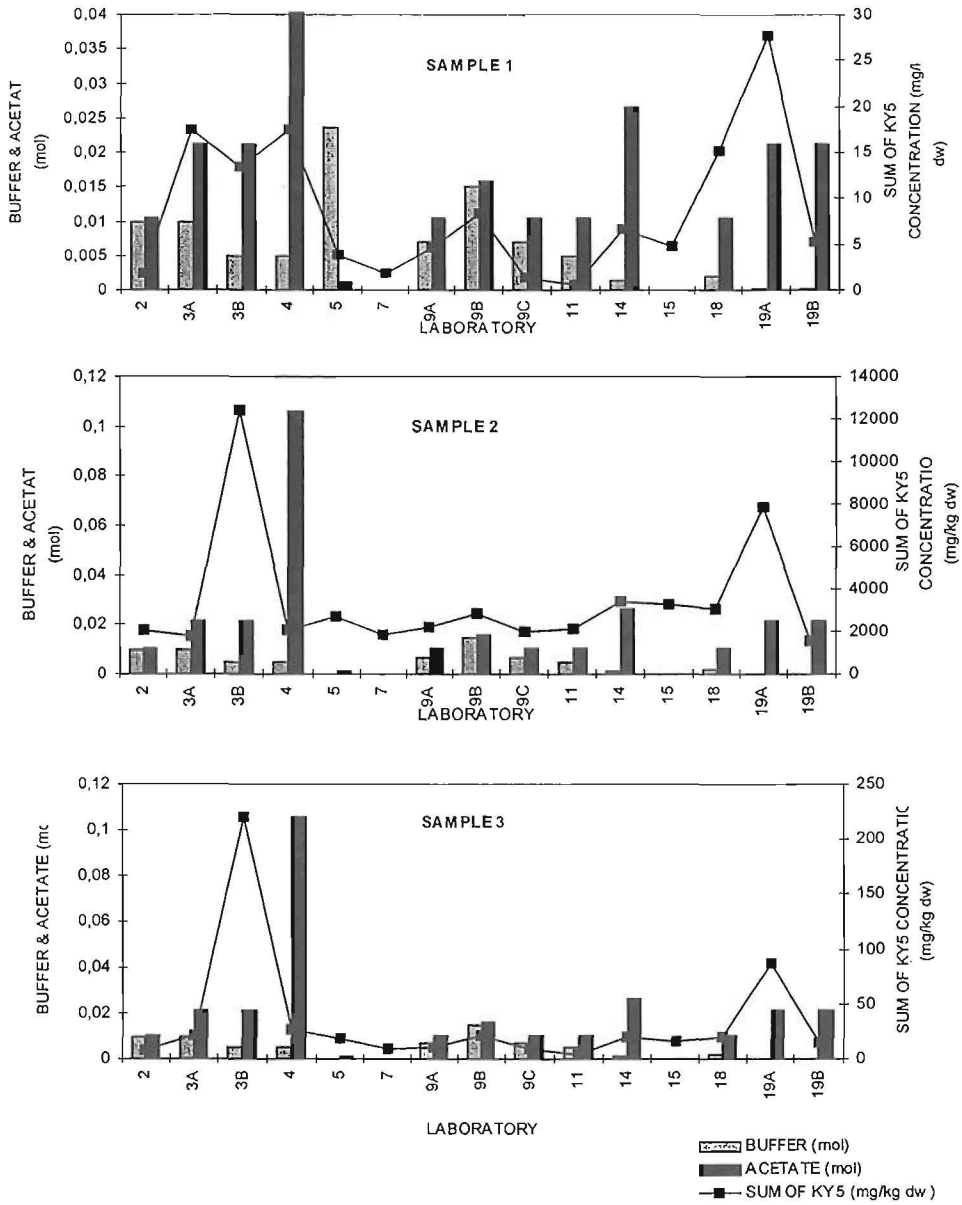
SAMP-LE	Compound	Chlorinated phenol as internal standard			Brominated phenol as internal standard		
		average	stdev	Cv%	average	stdev	Cv%
Sample 1	246-TCP	0.328	0.280	85.4	0.197	0.235	119.2
	2346-TeCP	6.528	4.393	67.3	4.827	5.331	110.4
	PCP	3.361	2.367	70.4	3.190	2.691	84.3
Sample 2	246-TCP	8.650	3.468	40.1	8.748	12.33	140.9
	2346-TeCP	385	442	114.7	419	465	111.0
	PCP	3197	3215	100.6	3035	1381	45.5
Sample 3	246-TCP	0.393	0.221	56.2	0.324	0.431	132.9
	2346-TeCP	22.5	32.0	142.6	13.6	13.6	99.9
	PCP	21.8	40.2	184.5	9.58	9.14	95.4

It seems that different internal standards do not have very big influence on the results. Bromophenols give just a little higher results but the difference is not remarkable. Single great discrepancies are not due to the chosen internal standard but rather due to the method.

3.3 Influence of acetylation procedure

In diagram 1 the amounts of acetylation reagent and used buffer solution were compared with the calculated results. Reagents were compared with the sum of three main components of chlorophenols, namely 2,4,6-tri-, 2,3,4,6-tetra- and pentachlorophenol. The results did not show any pattern. Very small amount of acetylation reagent gave extremely great concentrations and vice versa. So far the amounts of reagents seem not to influence the results.

Diagram 1. Influence of acetylation reagent and buffer solution to results.



3.4 Different methods

3.4.1 Extraction with acetic acetone

There were four laboratories that used acidic acetone extractions. Laboratory 951019 used the same method in both cases but the internal standards were different. Differences in results can be due to the calibration used. Otherwise the results of acidic acetone extractions were quite similar and also the recovery percentages.

3.4.2 Extraction with acetone-hexane

There was only two laboratories using acetone-hexane extraction and comparing them is not easy, especially as the results differ quite a lot. For sample 1 the results are quite

similar but in high concentration sample 2 results differ remarkably. Also for the spiked sample 3 the results differ and also recoveries.

3.4.3 Extraction with base

The results of basic extractions from different laboratories were variable and also the recoveries were not alike. For example only one laboratory of these found 3,4,5-trichlorophenol in sample 3. On the other hand all laboratories had not even examined this compound.

3.4.4 Extraction with carbonate

Carbonate extraction and then straight acetylation had been done in three laboratories. Results for samples 1 and 3 are quite similar in all laboratories but in high concentration sample 2 there are differencies. Recovery percentages are quite small and they vary in different laboratories quite a lot.

3.4.5 Extraction with solvent

The results of solvent extractions are externally quite similar with one exeption. But the recovery percentages are different.

3.4.6 Summary of extractions

It is clear that all these extractions are different but there are no clear trend that any extraction would be better than the other. The choise of one extraction procedure for standardization and future research should still be considered carefully.

4 SUMMARY

The relative standard deviation for all compounds ranged from 44.8% to 283.5% when more than two results were reported. For 246-TCP, 2346-TeCP and PCP relative standard deviations ranged from 75.3% to 283.5% when all results were examined. When outliers were excluded then RSD changed to be it was from 50.9% to 198.5%. There was no clear correlation between the extraction method used and the result obtained.

When evaluating the results of this ringtest it is a problem that we do not know the real concentrations of the samples. Recovery samples of course give some information, but there has been problems in sample 3. Somehow 2,4,6- trichlorophenol is either binding to or evaporating from the soil because the recovery percentages are so small despite of the extraction method used.

Appendix 1. Participating laboratories in alfabetical order

Geologian tutkimuskeskus, Kemian laboratorio, Kuopio, Finland

Helsingin kaupungin ympäristökeskus, Laboratorio, Helsinki, Finland

Helsingin yliopisto, Soveltavan kemian ja mikrobiologian laitos, Helsinki, Finland

Institutet för Vatten- och Luftvårdsforskning, Stockholm, Sweden

Joensuun yliopiston Karjalan tutkimuskeskus, Joensuu, Finland

Jyväskylän yliopiston ympäristöntutkimuskeskus, Jyväskylä, Finland

Kansanterveyslaitos, Kuopio, Finland

Lahden kaupungin valvonta- ja tutkimuslaboratorio, Lahti, Finland

Miljölaboratoriet, Nyköping, Sweden

Novalab Oy, Karkkila, Finland

Pohjois-Suomen Vesitutkimustoimisto, Oulu

Suomen ympäristökeskus, laboratorio, Helsinki

Valtion teknillinen tutkimuskeskus, Kemian tekniikka, Espoo

Appendix 2. Analytical methods used by the participating laboratories

LAB NR	951002	951003/A	951003/B	951004	951005	951006	951007	951009
Extraction								
Sample volume	about 3g	5 - 30g (depending on sample)	5 - 10g (depending on sample)	1-5g wet sample	0.2-0.5g	25 - 50g /about 25ml of solvent	12 - 25g (depending on sample)	2g
Solvent	0.1 M K2CO3 2*50ml	0.5M NaOH 50ml	hexane : acetone : dietylether : petrolether (2,5 : 5,5 : 1 : 9)	metanol : KOH(6M), (1 : 1), 3ml/g sample + askorbinacid as antioksidant	asetonitril 1.5ml	5% aceticacid in methanol 80ml + 10g Na2SO4	acidic ether n. 100ml	acetone:hexane (1:1)
ISTD	236-TCP	236-TCP	236-TCP	236-TCP	24-DBrP, 246-TBrP, TBr-o-Cresol, TBrGuaiacol	ESTD	2,4,6-tribromobiphenyl	246-TBrP
Extraction equipment	shaker	mixing with glas stick	Soxhlett apparatus	50ml:n kierrekorkillisissa koeputkissa ultraäänisauvalla	ultrasonic bath	Soxhlett apparatus	ultrasonic bath	ultrasonic bath
Time	30 min	2 days	6 h	5 min	5 min + standing in cold overnight	4 h	15min + standing overnight	6*2min during 1h
Purification								
Method				extraction	purification in column	filtration		extraction
Derivatization								
Reagent	acetic andyhride	acetic andyhride	acetic andyhride	acetic andyhride	acetic andyhride + pyridine		acetic andyhride	acetic andyhride
Volume	1 ml	2 ml	2 ml	2-10ml	125 ul + 50 ul			1ml
Time	5 min shaking	shaking until no gas	shaking until no gas	shaking	warming 75oC for 20min			2min shaking + 10min standing
Buffer		H2O + K2CO3	0,1M K2CO3	72%(w/v) K2CO3	0.8M K2CO3			0,1M K2CO3

LAB NR	951002	951003/A	951003/B	951004	951005	951006	951007	951009
Equipment								
Apparatus	MICROMAT HRGC 412	MICROMAT HRGC 412	MICROMAT HRGC 412	HP-5890 + autosampler HP 3763	Varian 3700 Model GC + Model Varian 8000 Autosampler	HPLC-apparatus Waters, pumps 510, Wisp 712	HP 5890 series II Plus, autosampler	HP 5890 series II, autosampler
Columns	NB-54 & NB-1701	NB-54 & NB-1701	NB-54 & NB-1701	J&W DB-17 & J&W DB-1	J&W DB-5 (30m, ID 0.25mm, film thickness 0.25um)	Novapak C18 3,9*150 mm	SP5-5, 30m, 0.25um, 0.25mm ID; SP5-35, 30m, 0.25um, 0.25mm ID	HP1 & HP5
Detectors	2* ECD	2* ECD	2* ECD	2*ECD	ECD	diodi.detektor 996	2*ECD	2*ECD
Carrier gas	Helium 4.5	Helium	Helium	Helium	high purity helium	******	Hydrogen	Helium
Volume	Column 1: 2.1ml/min & Column 2: 2.4ml/min	1,7 ml/min (20oC)	1,7 ml/min (20oC)	2 ml/min	20 cm/s, split ratio 1:10	******		1 ml/min
Make up gas	Argon/Methane	Argon/Methane	Argon/Methane	Argon/Methane	high purity nitrogen	******	Argon/Methane	Argon/Methane
Volume	Column 1:27ml/min & Column 2: 26ml/min	25-30 ml/min	25-30 ml/min	40 ml/min	30 ml/min	******		65 - 80 ml/min
HPLC gases						Gradienttiajo (virtaus 1,1 ml/min): A-eluentti: 1% etikka MeOH:ssa, B-eluentti: 1% etikka H2O:ssa		

LAB NR	951009/B	951009/C	951011	951014	951015	951017	951018	951019/A&B
Extraction								
Sample volume	2g	2g	0.1-15g	8-34g of dry sample	about 50g	5,7 - 7,6g	1-2g	10g
Solvent	acidic acetone	0.1M K2CO3	0.1M K2CO3 50ml	acetone + hexane (50%+50%)	acidic acetone (100ml acetone + 5ml HCl)	toluene 150ml	1M NaOH 25ml + heksane 25ml	acetone 60ml (acidified pH=2 HCl:lla)
ISTD	246-TBrP	246-TBrP	236-TCP	24-DBrP	26-DBrP	radioactive labeled 24-DCP and PCP	236-TCP	236-TCP or 246-TBrP
Extraction equipment	ultrasonic bath + shaking overnight	ultrasonic bath	shaker	Soxhlett apparatus	ultrasonic bath	Soxhlett apparatus	ultrasonic bath	shaker (Gyllengamp)
Time	15min + 16h	10 min	30min	8 h (minimum)	20min	24 h	15 min	15min + standing in room temperature 12 h
Purification								
Method	extraction			Silica column (Millipore)		extraction according to EPA method 3510		
Derivatization								
Reagent	acetic andyhride	acetic andyhride	acetic andyhride	acetic andyhride	acetic andyhride		acetic andyhride	acetic andyhride
Volume	1,5ml	1ml	1ml	2.5ml	???		1 ml	2ml
Time	½min shaking + 10min standing	10min	5min shaking + 5min standing		5min shaking + ½ h standing		5min shaking	vigorous mixing 1min + standing 12 h
Buffer	0,1M K2CO3			0.1M K2CO3 + heksaani	Na2CO3		0.1 M K2CO3	0.1M NaHCO3 + 0.2M NaOH , pH=9.9

LAB NR	951009/B	951009/C	951011	951014	951015	951017	951018	951019/A&B
Equipment								
Apparatus	HP 5890 series II, autosampler	HP 5890 series II, autosampler	HP 5890 Series II	HP 5890 Series II	Micromat HRGC 412 + autosampler CTC A2005	Gaschromatograph HP 5890 and mass spektrometer HP 5988	HP 5890 II + autosampler	HP 5890 (GC) + HP 5970 (MSD) + 7673 autosampler
Columns	HP1 & HP5	HP1 & HP5	DB-5, 30m, IDmm 0.25, filmi 0.25 microns	ULTRA 2, 5% PhMeSil (25m*0.32mm)	1) NB-54, 25m, halk. 0.32/0.4 mm, faasi 0.25um 2) NB-1701, 25m, halk. 0.32/0.4 mm, faasi 0.25um	DB 5, 60m*0,32mm, 0,25um	DB 5.625 (HP-5) , 30m, Ip 0.252mm, film 0.25um	HP-5 (25m*0.2mm, 0.33um)
Detectors	2*ECD	2*ECD	HP MS 5971 Series	ECD	2*ECD	Massaspektrometri EI/SIM	ECD + HP-massaselektiivinen detektori	MSD kvant.ionit 128, 162, 196, 232, 266, 330 (TBP)
Carrier gas	Helium	Helium	Helium	Helium	Helium	Helium	Nitrogen	Helium
Volume	1 ml/min	1 ml/min	80ml/min		1,30 ml/min		1 ml/min	33ml/min
Make up gas	Argon/Methane	Argon/Methane		Argon/Methane	Argon/Methane		Nitrogen	
Volume	65 - 80 ml/min	65 - 80 ml/min			26 ml/min		10 ml/min	
HPLC gases								

Appendix 3. Chlorophenol results of all laboratories

Lab nr	Sample	951002	951003A	951003B	951004	951005	951006	951007	951009	951011	951014	951015	951017	951018	951019A	951019B	N	AVERAGE	STDEVP	Cv%
3-CP	1													0,02			1	0,02	0,00	0,0
	2																0			
	3													0,02			1	0,02	0,00	0,0
26-DCP	1		0,44	0,58		0,07			0,02	0,00							5	0,22	0,24	109,7
	2		6,80			0,33			0,11	0,00			0,04				5	1,46	2,67	183,7
	3		0,12			0,10			0,02	0,00							4	0,06	0,05	85,1
24-DCP	1		0,24	0,07		0,03			0,02	0,00	0,05		0,07	0,15			8	0,08	0,07	92,1
	2		2,20			0,54			0,53	0,28	2,19	0,88	1,99	2,02	10,59	2,15	10	2,34	2,85	122,0
	3		0,34	0,14		0,04			0,02	0,01	0,09		0,06	0,08			8	0,10	0,10	103,9
35-DCP	1								0,00				0,01				2	0,01	0,01	74,3
	2								0,35				0,15		1,72	0,35	4	0,64	0,63	98,0
	3								0,01				0,01				2	0,01	0,00	30,0
23-DCP	1					0,08											1	0,08	0,00	0,0
	2					0,69											1	0,69	0,00	0,0
	3					0,12											1	0,12	0,00	0,0
34-DCP	1					0,10			0,00				0,07	0,07			4	0,06	0,04	60,1
	2					1,07			0,76			0,89	2,20	0,94			5	1,17	0,52	44,8
	3					0,09			0,01			0,16	0,06	0,03			5	0,07	0,05	79,1
246-TCP	1	0,05	0,45	0,39	0,31	0,07	1,30	0,06	0,07	0,04	0,16	0,11	0,24	0,91	0,76	0,15	15	0,34	0,36	107,2
	2		7,40	13,00	10,90	2,70	8,10		1,95	2,16	5,51	5,60	7,37	10,60	38,67	7,84	13	9,37	9,06	96,7
	3		0,41	0,76	0,37	0,13	1,00	0,09	0,09	0,06	0,25	0,16	0,24	0,54	1,37	0,22	14	0,41	0,37	92,3
236-TCP	1																0			
	2					0,09							0,07				2	0,08	0,01	17,5
	3																0			
235-TCP	1																0			
	2												0,02			1,56	2	0,79	0,77	96,8
	3																0			
245-TCP	1				0,03	0,04			0,01	0,00			0,03	0,08			6	0,03	0,02	75,7
	2				0,53	0,51			0,24	0,17	1,07	0,54	0,91	1,07	5,71	1,16	10	1,19	1,54	129,6
	3				0,06	0,05			0,01	0,01	0,05	0,02	0,03	0,04			8	0,03	0,02	52,5
234-TCP	1								0,00				0,01	0,02			3	0,01	0,00	53,6
	2					0,13			0,08				0,15	0,62			4	0,24	0,22	89,2
	3								0,01				0,01	0,02			3	0,01	0,00	46,4
345-TCP	1					0,07		0,04	0,09				0,13	0,08	1,59	0,30	7	0,33	0,52	159,1
	2					0,51			4,37			0,80	1,03	0,82	21,88	4,43	7	4,84	7,14	147,6
	3					1,10		1,60	1,17			2,00	1,79	1,30	8,01	1,30	8	2,28	2,18	95,7
2356-TeCP	1												0,01				1	0,01	0,00	0,0
	2					0,23								3,96			2	2,10	1,87	89,0
	3												0,01	0,04			2	0,02	0,02	76,5
2346-TeCP	1	1,01	10,50	9,20	10,86	2,30	5,10	0,89	2,54	0,37	2,88	2,30	4,11	10,40	17,52	3,35	15	5,56	4,81	86,5
	2	117,00	290,00	1450,00	201,27	145,00	170,00	180,00	99,15	82,94	592,00	270,00	173,00	252,00	1491,35	302,20	15	387,73	440,99	113,7
	3	4,66	14,30	100,00	17,11	10,40	9,80	4,80	5,47	2,13	9,20	7,50	4,18	11,41	46,48	7,57	15	17,00	24,43	143,7
2345-TeCP	1					0,02		0,02	0,02			0,02	0,01	0,11			6	0,03	0,03	94,1
	2					1,50			1,28			1,50		26,90	7,21	1,46	6	6,64	9,30	140,1
	3					0,03			0,04			0,04	0,01	0,09			5	0,04	0,03	62,8
PCP	1	0,73	6,60	3,90	6,37	1,54	1,80	0,97	2,05	0,24	3,59	2,40	3,43	3,89	9,40	1,80	15	3,25	2,44	75,3
	2	1990,00	1450,00	11000,00	1849,43	2540,00	1500,00	1700,00	2081,90	2074,00	2853,00	3000,00	2090,00	2742,00	6291,94	1274,97	15	2962	2440	82,4
	3	2,78	6,30	120,00	9,02	7,03	5,90	2,60	4,59	2,19	10,50	5,60	3,41	700,00	31,25	5,09	15	61,1	173	283,5

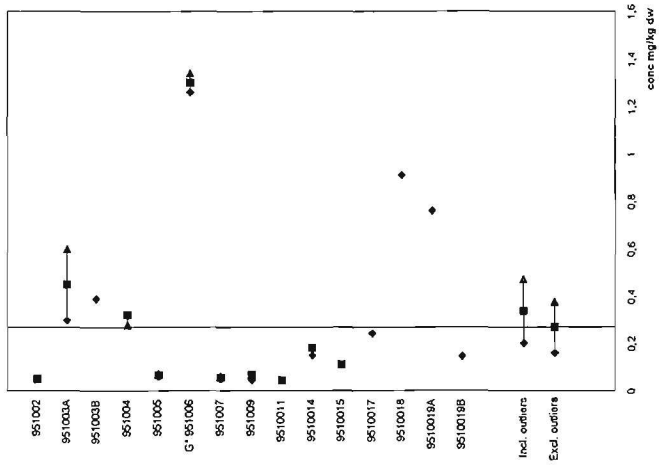
Appendix 4. Line diagrams of most frequently analysed chlorophenols

2,4,6-trichlorophenol

Sample 1

LAB	1	2	3	n	Izl-value	average
951002	0,05	0,05	0,05	3	0,8	0,050
951003A	0,3	0,45	0,6	3	0,3	0,450
951003B	0,39			1	0,1	0,390
951004	0,3204	0,3218	0,2788	3	0,1	0,307
951005	0,061	0,067	0,073	3	0,7	0,067
951006	1,26	1,3	1,34	3	2,6	
951007	0,0515	0,055	0,0585	3	0,8	0,055
951009	0,046	0,067	0,063	3	0,7	0,059
9510011		0,0437		1	0,8	0,044
9510014	0,15	0,18		2	0,5	0,165
9510015		0,11		1	0,6	0,110
9510017	0,244			1	0,2	0,244
9510018	0,91			1	1,5	0,910
9510019A	0,761			1	1,1	0,761
9510019B	0,146			1	0,5	0,146

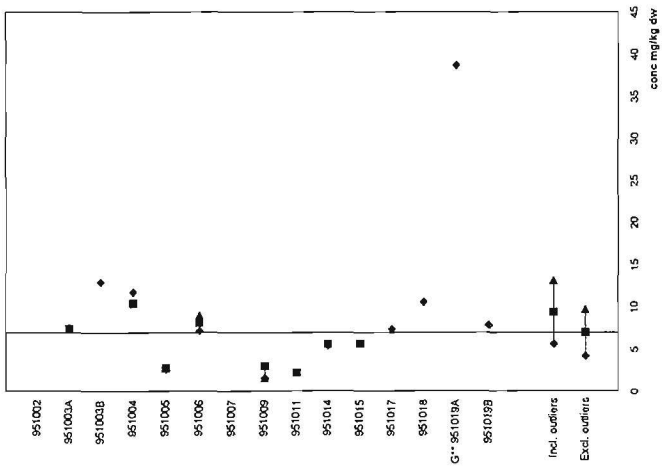
No. of laboratories:	15
No. of laboratories included in the calculations (p):	14
Mean (m):	0,268
Standard deviation (STD):	0,275
CV%:	102,5



Sample 2

LAB	1	2	3	n	Izl-value	average
951002					1,0	
951003A	7,24	7,4	7,56	3	0,2	7,40
951003B	13			1	0,4	13,0
951004	11,8107	10,4313	10,4708	3	0,2	10,9
951005	2,592	2,7	2,808	3	0,7	2,70
951006	7,2	8,1	9	3	0,1	8,10
951007					1,0	
951009	1,575	2,97	1,611	3	0,8	2,05
9510011		2,16		1	0,8	2,16
9510014	5,44	5,57		2	0,4	5,51
9510015		5,6		1	0,4	5,60
9510017	7,37			1	0,2	7,37
9510018	10,6			1	0,1	10,6
9510019A	38,666			1	3,1	
9510019B	7,835			1	0,2	7,84

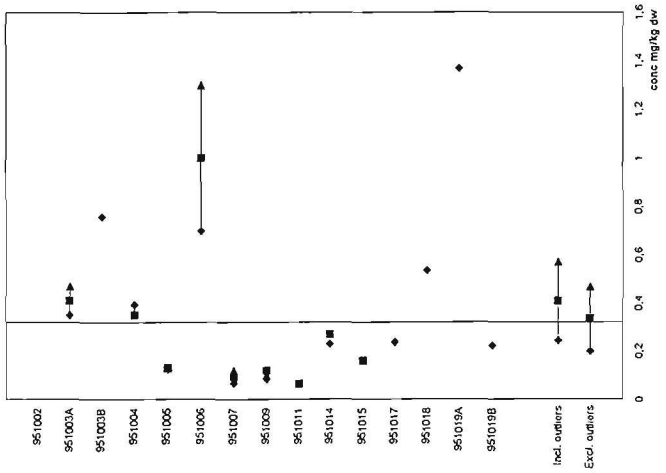
No. of laboratories:	13
No. of laboratories included in the calculations (p):	12
Mean (m):	6,94
Standard deviation (STD):	3,53
CV%:	50,9



Sample 3

LAB	1	2	3	n	Izl-value	average
951002					1,0	
951003A	0,35	0,41	0,47	3	0,0	0,410
951003B	0,76			1	0,9	0,760
951004	0,394	0,351	0,359	3	0,1	0,368
951005	0,123	0,13	0,137	3	0,7	0,130
951006	0,7	1	1,3	3	1,5	1,00
951007	0,066	0,092	0,118	3	0,8	0,092
951009	0,084	0,118	0,1	3	0,8	0,101
9510011		0,0643		1	0,9	0,064
9510014	0,23	0,27		2	0,4	0,250
9510015		0,16		1	0,6	0,160
9510017	0,236			1	0,4	0,236
9510018	0,535			1	0,3	0,535
9510019A	1,389			1	2,5	
9510019B	0,223			1	0,5	0,223

No. of laboratories:	14
No. of laboratories included in the calculations (p):	13
Mean (m):	*0,333*
Standard deviation (STD):	0,283
CV%:	84,9



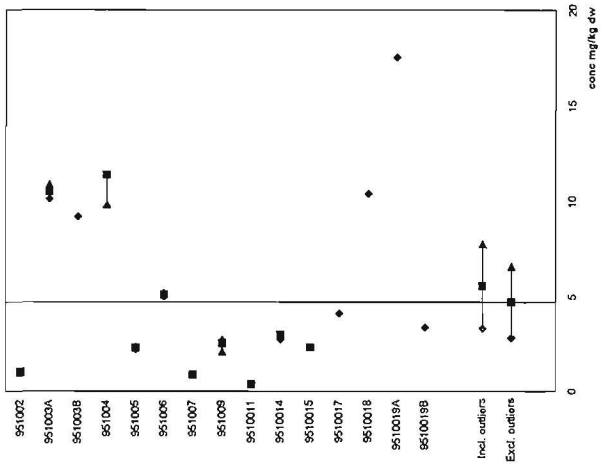
2,3,4,6-tetrachlorophenol

Sample 1

LAB	1	2	3	n	Izl-value	average
951002	1	1,04	0,99	3	0,9	1,01
951003A	10,12	10,5	10,88	3	1,0	10,5
951003B	9,2			1	0,7	9,20
951004	11,35	11,39	9,84	3	1,1	10,9
951005	2,245	2,3	2,355	3	0,7	2,30
951006	5	5,1	5,2	3	0,1	5,10
951007	0,89	0,89	0,89	3	0,9	0,89
951009	2,709	2,542	2,122	3	0,6	2,46
9510011		0,371		1	1,0	0,371
9510014	2,77	2,99		2	0,5	2,88
9510015		2,3		1	0,7	2,30
9510017	4,11			1	0,3	4,11
9510018	10,4			1	1,0	10,4
9510019A	17,519			1	2,4	
9510019B	3,352			1	0,4	3,35

No. of laboratories: 15
No. of laboratories included in the calculations (p): 14

Mean (m): 4,695
Standard deviation (STD): 3,857
Cv%: 82,1

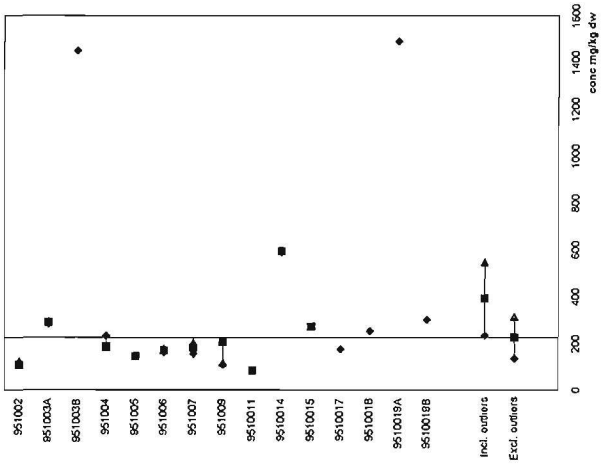


Sample 2

LAB	1	2	3	n	Izl-value	average
951002	119	108	123	3	0,6	117
951003A	284,3	290	295,7	3	0,2	290
951003B	1450			1	2,3	
951004	232,9	187,7	183,2	3	0,4	201
951005	143,1	145	146,9	3	0,5	145
951006	163	170	177	3	0,5	170
951007	156	180	204	3	0,5	180
951009	109,3	205,6	117,3	3	0,5	144
9510011		82,94		1	0,7	83
9510014	591	593		2	0,4	592
9510015		270		1	0,3	270
9510017	173			1	0,5	173
9510018	252			1	0,3	252
9510019A	1491			1	2,4	
9510019B	302,2			1	0,2	302

No. of laboratories: 15
No. of laboratories included in the calculations (p): 13

Mean (m): 224,5
Standard deviation (STD): 129,4
Cv%: 57,6

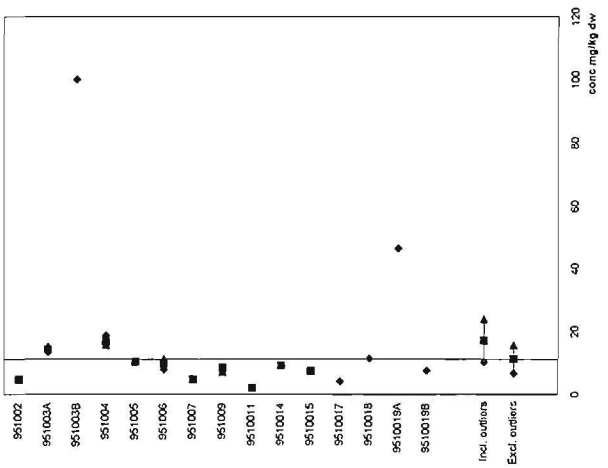


Sample 3

LAB	1	2	3	n	Izl-value	average
951002	4,61	4,73	4,65	3	0,5	4,66
951003A	13,35	14,3	15,25	3	0,1	14,3
951003B	100			1	3,3	
951004	18,76	16,78	15,8	3	0,0	17,1
951005	10,27	10,4	10,53	3	0,3	10,4
951006	8,1	9,8	11,5	3	0,3	9,80
951007	4,729	4,8	4,871	3	0,5	4,80
951009	7,421	8,533	7,296	3	0,4	7,75
9510011		2,13		1	0,6	2,13
9510014	9,2	9,21		2	0,3	9,21
9510015		7,5		1	0,4	7,50
9510017	4,18			1	0,5	4,18
9510018	11,41			1	0,2	11,4
9510019A	46,476			1	1,2	46,5
9510019B	7,568			1	0,4	7,57

No. of laboratories: 15
No. of laboratories included in the calculations (p): 14

Mean (m): 11,24
Standard deviation (STD): 10,92
Cv%: 97,2



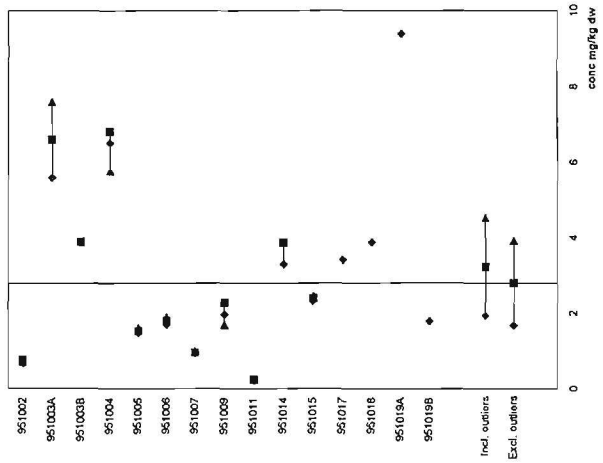
Pentachlorophenol

Sample 1

LAB	1	2	3	n	Izl-value	average
951002	0,69	0,77	0,72	3	1,0	0,727
951003A	5,6	6,6	7,6	3	1,3	6,60
951003B		3,9		1	0,3	3,90
951004	6,51	6,81	5,78	3	1,2	6,37
951005	1,495	1,54	1,615	3	0,7	1,55
951006	1,7	1,8	1,9	3	0,6	1,80
951007	0,949	0,97	0,991	3	0,9	0,970
951009	1,98	2,29	1,71	3	0,5	1,99
951011	0,218	0,239	0,26	3	1,2	0,239
951014	3,31	3,87		2	0,1	3,59
951015	2,33	2,4	2,47	3	0,3	2,40
951017	3,43			1	0,1	3,43
951018	3,89			1	0,3	3,89
951019A	9,396			1	2,4	
951019B	1,7978			1	0,6	1,80

No. of laboratories: 15
No. of laboratories included in the calculations (p): 14

Mean (m): 2,804
Standard deviation (STD): 1,945
Cv%: 69,4

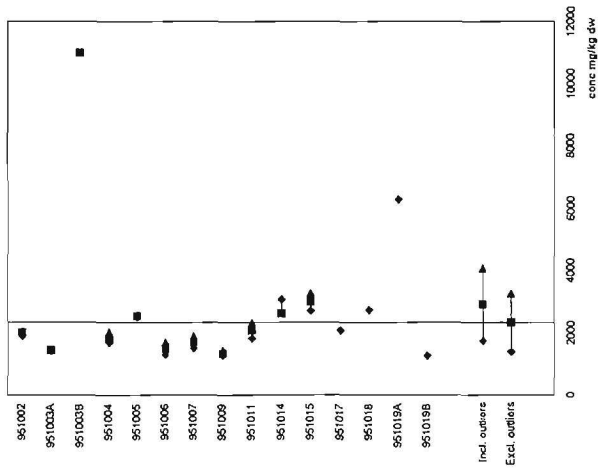


Sample 2

LAB	1	2	3	n	Izl-value	average
951002	1910	2020	2040	3	0,4	1990
951003A	1427	1450	1473	3	0,6	1450
951003B		11000		1	3,2	
951004	1697,9	1820	2030,4	3	0,4	1849
951005	2508	2540	2572	3	0,1	2540
951006	1300	1500	1700	3	0,6	1500
951007	1510	1700	1890	3	0,5	1700
951009	1288	1329	1420	3	0,6	1346
951011	1825	2074	2323	3	0,3	2074
951014	3077	2629		2	0,0	2853
951015	2720	3000	3280	3	0,0	3000
951017	2090			1	0,3	2090
951018	2742			1	0,1	2742
951019A	6291,94			1	1,3	6292
951019B	1274,971			1	0,6	1275

No. of laboratories: 15
No. of laboratories included in the calculations (p): 14

Mean (m): 2336
Standard deviation (STD): 1272
Cv%: 54,5

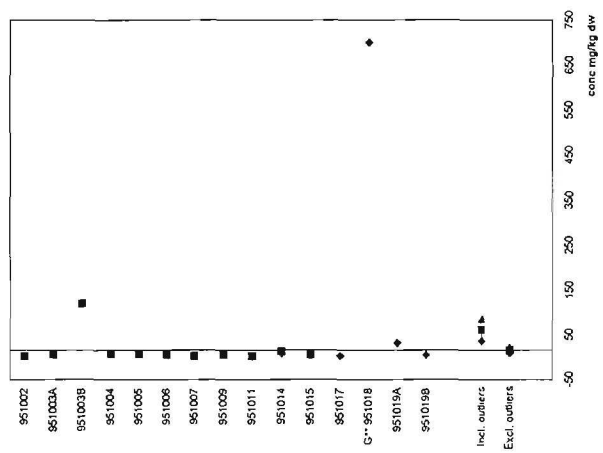


Sample 3

LAB	1	2	3	n	Izl-value	average
951002	2,73	2,86	2,74	3	0,3	2,78
951003A	5,92	6,3	6,68	3	0,3	6,30
951003B		120		1	0,3	120
951004	9,63	8,82	8,6	3	0,3	9,02
951005	6,952	7,03	7,108	3	0,3	7,03
951006	5,8	5,9	6	3	0,3	5,90
951007	2,529	2,6	2,671	3	0,3	2,60
951009	6,35	6,43	6,29	3	0,3	6,36
951011	1,776	2,19	2,604	3	0,3	2,19
951014	8,82	12,2		2	0,3	10,51
951015	5,35	5,6	5,85	3	0,3	5,60
951017	3,41			1	0,3	3,41
951018	700			1	3,6	
951019A	31,2512			1	0,2	31,25
951019B	5,0887			1	0,3	5,09

No. of laboratories: 15
No. of laboratories included in the calculations (p): 14

Mean (m): 15,57
Standard deviation (STD): 30,92
Cv%: 198,5



PART II

Analysis of chlorophenols in contaminated soil 1996

INTER-LABORATORY TEST OF METHODS DESCRIBED IN THE REPORT
"NORDIC GUIDELINE FOR CHEMICAL ANALYSIS OF
CONTAMINATED SOIL SAMPLES"

CONTENTS

1. Introduction

This inter-laboratory test is connected to the Nordtest project 1143-93 "Nordic Guidelines for Chemical Analysis of Contaminated Soil Samples" and 1286-96 "Validation and testing of chemical analysis of contaminated soil". This guideline contains analyzing methods for the most common contaminants in soil. In this inter-laboratory test these methods have been tested in different laboratories in the Nordic countries. The inter-laboratory test concerning chlorophenols in contaminated soil was arranged by the laboratory of Finnish Environment Institute.

2. Participating laboratories

Invitation to participate in the test was sent to most laboratories dealing with environmental samples in the Nordic countries. Chlorophenol samples were sent to 29 laboratories and twenty of these replied with an answering percent of 69%. These twenty laboratories were from Denmark (4), Finland (10), Norway (1) and Sweden (5). The participating laboratories are listed in alfabetical order in appendix 1. All of these twenty laboratories analyzed the samples with the proposed Nordtest method and eight laboratories also with their own method.

3. Samples

Samples were sent to the participating laboratories 22nd of April 1996. There were three soil samples (A, B, and C) and one solution (D). Soil samples were prepared from authentic soil from a saw mill site in Finland contaminated with chlorophenols. Two of these samples contained low concentrations and one contained quite high concentrations of different chlorophenols.

The soil samples were field moist, sieved through an 8 mm sieve and homogenized by hand in the laboratory. All laboratories had to report the results calculated to dry weight. The laboratory that prepared the samples found the dry matter content to be 80.0 %, 78.9 % and 75.6 % for samples A, B and C, respectively. The organic matter content was 5.3 %, 5.6 % and 9.3 % (wt/dry wt) for samples A, B and C, respectively. Sample A was of the same batch as sample B, but it was spiked with 2 mg/kg of 2,4,6 trichlorophenol (TCP), 2 mg /kg of 2,3,4,6-tetrachlorophenol (TeCP), and 5 mg/kg of pentachlorophenol (PCP). The soil samples had a natural content of more than 16 different chlorophenol congeners. The solution D was prepared by mixing known amounts of 16 different chlorophenols in water which was botteled to small vials. The homogeneity of the samples were tested and the coefficient of variation varied between 1.3 % and 21.6 % (Table 1).

Table 1. Homogeneity of samples used in the inter-laboratory test (n=5-10)

Sample	246-TCP		2346-TeCP		PCP	
	mean conc. A,B,C mg/kg dw D mg/l	CV_R %	mean conc. A,B,C mg/kg dw D mg/l	CV_R %	mean conc. A,B,C mg/kg dw D mg/l	CV_R %
A (Soil)	0.188	8.2	1.95	9.6	4.88	12.2
B (Soil)	0.077	18.3	2.81	21.6	1.38	15.8
C (Soil)	0.743	2.3	208	10.3	1500	6.7
D (Solution	47.8	4.1	47.6	1.3	171	5.0

4. Results of the interlaboratory test

The laboratories were asked to analyze 3 subsamples from each sample. Several laboratories reported the results for up to 16 different chlorophenol congeners, but the main part only reported results for 2,4,6-trichlorophenol, 2,3,4,6-tetrachlorophenol and pentachlorophenol. The statistical treatment has been done according to the international standard ISO 5725-2: "Accuracy (trueness and precision) of measurement methods and results. Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method."

This involves the testing of the within-laboratory standard variances by Cochran's test and the testing of the variation of means by Grubb's test after which statistical outliers are excluded for the final calculation of the repeatability and reproduciblity of the method. The number of data in many cases do not allow statistical handling of the data for all compounds.

4.1 Proposed Nordtest method

The laboratories analyzed from three to sixteen chlorophenols with recommended Nordtest method. Most laboratories analyzed only few of the most important compounds. For this reason we could not do the statistical handling for some compounds.

A summary of the results is given in Table 2 and all the test results are given in appendix 2. Line diagrams of mostly analysed chlorophenols are presented in appendix 3.

Ranges of CV_r :

Sample A from 9.4 % (PCP) to 25.5 % (24-DCP)
Sample B from 12.2 % (2346-TeCP) to 94.4 % (2345-TeCP)
Sample C from 8.2 % (24-DCP) to 19.8 % (2346-TeCP)
Solution D from 3.7 % (235-tcp) to 8.6 % (34-DCP)

Ranges of CV_R :

Sample A from 31.6 % (24-DCP) to 58.3 % (34-DCP)
Sample B from 31.4 % (24-DCP) to 90.2 % (2345-TeCP)
Sample C from 12.9 % (PCP) to 71.1% (246-TCP)
Solution D from 7.9 % (35-DCP) to 48.0 % (236-TCP)

Table 2. The summary of test results (proposed Nordtest method). Samples A, B, C mg/kg dry weight, solution D mg/l.

Chloro-phenol	Sample	N	p	Ex-pected level (mg/l)	Mean (mg/kg dm.)	Mean (mg/l)	Accuracy (%)	s_r	CV_r (%)	s_R	CV_R (%)
23-DCP	Sample A	6	1								
	Sample B	6	1								
	Sample C	6	1								
	Sample D	6	6	40		31.4	78.5				
24-DCP	Sample A	8	7		0.029			0.007	25.6	0.009	31.6
	Sample B	8	7		0.025			0.004	14.9	0.008	31.4
	Sample C	8	6		0.362			0.030	8.2	0.250	69.2
	Sample D	12	10	40		47.2	118.0	3.10	6.6	14.4	30.5
24/25-DCP	Sample A	5	5		0.040						
	Sample B	5	5		0.043						
	Sample C	5	3		0.340						
	Sample D	3	3	80		67.9	84.9				
25-DCP	Sample A	1	0								
	Sample B	1	0								
	Sample C	1	0								
	Sample D	2	2	40							
26-DCP	Sample A	6	2		0.012						
	Sample B	6	2		0.010						
	Sample C	6	1								
	Sample D	10	10	40		35.9	89.7	1.99	5.6	7.42	20.7
34-DCP	Sample A	8	7		0.039			0.008	19.5	0.023	58.3
	Sample B	9	6		0.037			0.027	72.0	0.028	76.1
	Sample C	10	9		0.327			0.037	11.4	0.183	55.8
	Sample D	10	9	40		31.8	79.4	2.74	8.6	5.96	18.8
35-DCP	Sample A	7	5		0.011						
	Sample B	7	5		0.023						
	Sample C	7	5		0.118						
	Sample D	7	7	40		35.1	87.8	1.97	5.6	2.79	7.9
234-TCP	Sample A	5	2								
	Sample B	5	3		0.011						
	Sample C	7	7		0.066						
	Sample D	9	9	40		32.5	81.2	1.64	5.1	5.44	16.8
235-TCP	Sample A	6	1								
	Sample B	6	2		0.005						
	Sample C	6	3		0.075						
	Sample D	6	6	40		31.0	77.6	1.16	3.7	5.17	16.7
236-TCP	Sample A	5	2		0.019						
	Sample B	5	2		0.027						
	Sample C	7	4		0.264						
	Sample D	8	8	40		46.8	116.9	2.56	5.5	22.5	48.0
245-TCP	Sample A	12	9		0.029			0.005	15.6	0.013	45.6
	Sample B	12	9		0.023			0.005	23.2	0.008	34.6
	Sample C	11	10		0.281			0.029	10.4	0.149	53.0
	Sample D	13	11	40		44.2	110.4	2.02	4.6	7.95	18.0

continued

Chloro-phenol	Sample	N	p	Ex-pected level (mg/l)	Mean (mg/kg dm.)	Mean (mg/l)	Accuracy (%)	s_r	CV_r (%)	s_R	CV_R (%)
246-TCP	Sample A	18	16		0.253			0.027	10.6	0.081	31.8
	Sample B	17	15		0.083			0.014	17.0	0.034	40.8
	Sample C	16	13		1.98			0.244	12.4	1.40	71.1
	Sample D	17	14	60		53.4	89.0	2.80	5.2	9.26	17.3
345-TCP	Sample A	7	7		0.043			0.024	55.5	0.040	95.1
	Sample B	7	6		0.030			0.011	37.9	0.016	51.9
	Sample C	7	6		1.64			0.136	8.3	0.851	51.9
	Sample D	8	8	20		18.1	90.7	1.54	8.5	6.05	33.3
2345-TeCP	Sample A	10	8		0.015			0.002	13.1	0.006	41.8
	Sample B	10	7		0.021			0.020	94.4	0.019	90.2
	Sample C	9	9		0.658			0.076	11.5	0.356	55.5
	Sample D	11	10	20		19.5	97.6	0.855	4.4	3.92	20.1
2346-TeCP	Sample A	19	17		2.33			0.266	11.4	1.12	47.9
	Sample B	19	16		2.23			0.271	12.2	1.06	47.7
	Sample C	19	17		193			38.4	19.8	110	56.9
	Sample D	16	13	60		52.8	88.1	2.32	4.4	18.0	34.1
2356-TeCP	Sample A	3	0								
	Sample B	3	0								
	Sample C	3	1								
	Sample D	4	3	0							
PCP	Sample A	20	19		5.85			0.548	9.4	2.34	40.0
	Sample B	20	17		1.36			0.212	15.5	0.443	32.4
	Sample C	18	15		1418			183	12.9	646	12.9
	Sample D	17	14	200		158	78.9	12.7	8.1	51.9	32.9

4.2 Own method

There were eight laboratories that used their own analyzing method for chlorophenols. 246-TCP, 2346-TeCP and PCP were analyzed by all these laboratories and other compounds in smaller amount. For this reason statistical handling of outliers by Cochran's and Grubb's tests could not be performed with these results. The mean, reproducibility and repeatability are thus calculated according to ISO 5725-2 -standard including all the results.

The summary of results is given in Table 3 and all test results are in appendix 5. Line diagrams of 246-TCP, 2346-TeCP and PCP are presented in appendix 6.

Ranges of CV_r :

Sample A from 10.2 % (24-DCP) to 23.2 % (2345-TeCP)
Sample B from 11.5 % (246-TCP) to 48.7 % (PCP)
Sample C from 15.3 % (PCP) to 32.3 % (245-TCP)

Ranges of CV_R :

Sample A from 28.1 % (24-DCP) to 55.8 % (2346-TeCP)
Sample B from 36.6 % (245-TCP) to 132.3 % (PCP)
Sample C from 45.7 % (245-TCP) to 124.5 % (24-DCP)

Table 3. The summary of test results by own method (mg/kg dry weight). Please note that outliers are neither identified nor excluded.

Chlorophenol	Sample	N	p	Mean	sr	CVr (%)	sR	CVR (%)
23-DCP	Sample A	2						
	Sample B	2						
	Sample C	2						
24-DCP	Sample A	4	3	0.024	0.002	10.2	0.007	28.1
	Sample B	4	3	0.020	0.004	19.0	0.015	75.4
	Sample C	4	3	0.356	0.066	18.4	0.444	124.5
26-DCP	Sample A	3	2	0.002	0.000	19.9	0.001	36.5
	Sample B	3	1					
	Sample C	3	1					
34-DCP	Sample A	3	2					
	Sample B	3	1					
	Sample C	3	2					
234-TCP	Sample A	2	1					
	Sample B	2	1					
	Sample C	2	2					
235-TCP	Sample A	2	1					
	Sample B	2	1					
	Sample C	2	1					
245-TCP	Sample A	4	3			14.3	0.008	38.6
	Sample B	4	3	0.022	0.003	21.5	0.008	36.6
	Sample C	4	3	0.021	0.004	32.3	0.119	45.7
				0.260	0.084			
246-TCP	Sample A	8	8	0.366	0.082	22.5	0.198	54.2
	Sample B	7	6	0.080	0.009	11.5	0.043	53.9
	Sample C	7	6	1.35	0.244	18.1	1.069	79.4
2345-TeCP	Sample A	4	4	0.016	0.004	23.3	0.008	48.5
	Sample B	4	2	0.021				
	Sample C	4	4	0.096	0.197	20.5	0.714	74.4
2346-TeCP	Sample A	8	8	2.73	0.541	19.8	1.52	55.8
	Sample B	8	8	2.26	0.389	17.3	1.25	55.6
	Sample C	8	8	249	45.2	18.2	159	63.8
2356-TeCP	Sample A	2	1					
	Sample B	2	0					
	Sample C	2	1					
PCP	Sample A	8	8	6.23	1.29	20.8	3.29	52.7
	Sample B	7	7	1.91	0.931	48.7	2.53	132.3
	Sample C	7	7	1432	218	15.3	905	63.2

4.3 Differences between laboratories

It is difficult to compare the performance of the laboratories because they have analyzed the compounds so differently. Some laboratories have analyzed only the three main compounds (246-TCP, 2346-TeCP and PCP) and some all sixteen compounds. In table 4 has been calculated for every laboratory the number of results that was between +-25% and +-10% of the grand mean.

Table 4. Number of results obtained by the laboratories near the grand mean or the known concentration.

LAB	SAMPLE A (GRAND MEAN)			SAMPLE B (GRAND MEAN)			SAMPLE C (GRAND MEAN)			SAMPLE D (GRAND MEAN)			SAMPLE D (KNOWN AMOUNT)		
	SUM	±25%	±10%	SUM	±25%	±10%	SUM	±25%	±10%	SUM	±25%	±10%	SUM	±25%	±10%
1	9	4	1	8	4	1	11	2	2	15	11	7	15	9	1
2	3	3	2	2	2	2	1	1	0	0	-	-	0	-	-
3	8	3	2	8	3	3	7	1	0	11	7	4	11	6	4
4	8	2	1	10	3	0	9	0	0	12	7	3	12	4	0
5	10	3	1	12	4	3	12	3	3	14	14	10	14	14	0
6	The results of this laboratory are so different from others that they have been excluded from all calculations														
7	3	1	0	3	0	0	3	1	0	11	7	7	11	9	2
8	4	2	0	4	4	0	4	0	0	4	0	0	4	1	0
9	6	5	2	6	3	1	9	6	1	11	7	2	11	5	2
10	2	1	0	2	2	0	2	2	2	6	3	2	6	5	3
11	8	5	3	7	1	0	10	8	3	13	10	6	13	9	2
12	3	0	0	3	1	1	2	0	0	3	0	0	3	0	0
13	5	1	0	5	1	0	0	-	-	6	2	1	6	2	0
14	11	5	2	10	0	0	9	4	3	14	4	3	14	11	4
15	6	0	0	6	2	1	7	2	0	9	6	6	9	6	1
16	3	1	1	2	0	0	2	1	0	0	-	-	0	-	-
17	6	1	1	7	2	0	10	1	1	15	8	6	15	13	11
18	9	4	2	9	8	1	9	2	0	0	-	-	0	-	-
19	4	3	1	4	2	0	4	0	0	4	2	1	4	2	1
20	2	0	0	2	1	0	2	0	0	3	2	2	3	2	0

5. Conclusions

The repeatability coefficient (CV_r) for soil samples varied from 8.2% to 94.9%. The biggest variation was with compounds in small concentrations. The bigger concentration the better repeatability. The reproducibility variation coefficient (CV_R) for soil samples varied from 12.9% to 90.2%. There was no correlation between the variation and the concentration level.

Although the results obtained by own method could not be statistically calculated properly we can see a difference between those results and results from the proposed Nordtest method. If we look upon own method results we can see that (CV_R) is for the three main components (246-TCP, 2346-TeCP, PCP) from 52.7% to 132.3% and for the proposed Nordtest method the same variation was from 12.9% to 71.1%. So reproducibility with Nordtest method is somewhat better than with own methods.

Solution D gave smaller repeatability results (from 3.7% to 8.6%) than actual soil samples and CV_R was from 7.2% to 48.0%. This was better than what was obtained for the soil samples, but not satisfactory results for the analysis of a rather simple sample solution.

The variation may be due to the fact that the laboratories used the tested method for the first time and thus had problems to find the right level of concentration. This problem can however, be overcome by better validation in separate laboratories. At present there are no commercial reference material available and the reason for the variation in the results in the soil samples apparently was not due the quality of the test material, but rather due to problems with the analytical performance.

6. References

International Standard ISO 5725-1 and ISO 5725-2 (1994): Accuracy (Trueness and Precision) of Measurement Methods and Results

Part 1: General Principles and Definitiions.

Part 2: Basic Method for the Determination of Repeatability and Reproducibility of a Standard measurement Method.

Kalevi, K. and Jørgensen, K.S. 1997. Analysis procedure for chlorophenols. In: Karstensen, K.H. (ed.) Nordic guideline for chemical analysis of contaminated soil samples. NORDTEST Technical Report 329. pp. 77 - 84. NORDTEST, Espoo, Finland.

Karstensen, K.H., Ringstad, O., Rustad, I., Kalevi, K., Jørgensen, K., Nylund, K., Alsberg, T., Olafsdottir, K., Heidenstam, O. and Solberg, H., 1998. Methods for chemical analysis of contaminated soil samples - tests of their reproducibility between Nordic laboratories. Talanta, vol 46, pp. 423-437.

Appendix 1. Participating laboratories in alfabetical order

Analycen Nordre Ab, Lidkøping, Sweden

Control And Recearch Laboratory, Lahti, Finland

Environmental Laboratory,city Of Helsinki, Helsinki, Finland

Finnish Environment Institute, Laboratory, Helsinki, Finland

Geological Survey Of Finland, Kuopio, Finland

Hygiejnisk Forvaltning, Aalborg Øst, Denmark

Institute For Environmental Research, Jyväskylä, Finland

Juvegroup Oy , Rovaniemi, Finland

Km Laboratorierna, Skara, Sweden

Levnedmiddelkontrollen I/s, Skovlunde, Denmark

Milab, Jørfølla, Sweden

Miljølaboratoriet I Nykøping Ab, Nykøping, Sweden

Miljø- Og Levnedsmiddelkontrollen, Helsingør, Denmark

National Public Health Institute, Kuopio, Finland

Pohjois-suomen Vesitutkimustoimisto, Oulu, Finland

Sintef, Miljøteknologi Og Analyse, Oslo, Norway

Steins Laboratorium, Brørup, Denmark

The City Of Tampere, Food And Environmental Laboratory, Tampere, Finland

Vtt Chemical Technology, Espoo, Finland

Vattenvårdslaboratoriet, Stockholm, Sweden

Appendix 2. Chlorophenol results of all laboratories with the recommended method

Compound	Sample	N	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
23-DCP	A	1	<0.01		<0.005		0,000						<0.01			<0.01				<0.01		
	B	2	<0.01		<0.005		0,000						<0.01			0,000				<0.01		
	C	2	<0.01		<0.005		0,000						<0.01			0,000				<0.01		
	D	6	23,5		27,4		32,6						28,2			39,1			40,0			
24-DCP	A	7	0,023		0,033			<0.1		0,036			0,027		0,019		0,037				0,028	
	B	7	0,023		0,035			<0.1		0,030			0,020		0,013		0,027				0,030	
	C	7	0,020		0,196			<0.1		0,717	0,420		0,280				0,537				0,217	
	D	11	29,9		74,4			112,8	56,3	31,3	37,4		58,7		53,0		53,7		40,0		37,8	
24/25-DCP	A	5				0,040	0,012									0,055			0,063	0,033		
	B	5				0,052	0,023									0,060			0,053	0,033		
	C	5				0,440	0,290									0,515			0,687	0,273		
	D	3				48,0	70,9									93,2						
25-DCP	A	0	<0.01																			
	B	0	<0.01																			
	C	0	<0.01																			
	D	2	33,4																41,0			
26-DCP	A	2	<0.01		<0.005		0,064						<0.01			0,010				<0.01		
	B	2	<0.01		<0.005		0,048						<0.01			0,010				<0.01		
	C	1	<0.01		<0.005		0,097						<0.01			<0.01				<0.01		
	D	10	34,0		50,6	27,3	33,9		34,0		31,3		31,0			47,5	35,7		38,0			
34-DCP	A	7	0,055		0,051	0,052	0,000	<0.1					0,020			0,060				0,043		
	B	7			0,035	0,061	0,021	<0.1					0,020			0,130			0,059	0,030		
	C	9	0,177		0,206	0,677	0,183	<0.1			0,377		0,250			0,430			0,503	0,177		
	D	10	28,8		30,7	29,0	33,7	59,6	30,0		25,6		30,9			46,4			37,5			
35-DCP	A	5	<0.01		0,014	0,051	0,004						<0.01			0,010				0,010		
	B	5	<0.01		0,011	0,068	0,006						<0.01			0,040				0,010		
	C	6	0,028		0,294	0,177	0,281						0,043			<0.01			0,060	<0.03		
	D	7	34,5		37,6	32,3	34,6		33,0							38,2			37,5			
234-TCP	A	3	0,013				0,000						<0.01			0,010				<0.01		
	B	3	0,013				0,006						<0.01			0,015				<0.01		
	C	7	0,062				0,043				0,067		0,070			0,075			0,097	0,050		
	D	9	31,5			27,7	32,6		36,7		24,2	40,5	33,7			29,5			40,0			
235-TCP	A	1	<0.01			<0.01	0,000						<0.01			<0.01				<0.01		
	B	3	0,010			0,017	0,000						<0.01			<0.01				<0.01		
	C	3	0,013			0,213	0,000						<0.01			<0.01				<0.01		
	D	6	28,2				32,9						30,6			22,2	32,7		39,5			

Compound	Sample	N	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
236-TCP	A	2	<0.01			0,034	0,004						<0.01							<0.01		
	B	2	<0.01			0,049	0,004						<0.01							<0.01		
	C	4	<0.01			0,970	0,005						<0.01				0,063		0,018	<0.01		
	D	8	7,1			33,7	32,2				51,9	73,0			61,7		63,7		66,0			
245-TCP	A	10	0,025		0,029		0,015				0,027		0,023		0,021	0,065	0,040		0,038	0,033		
	B	11	0,024		0,024	0,018	0,015	<0.1			0,023		0,017		0,019	0,120	0,040		0,036	0,027		
	C	10	0,263		0,215	0,050	0,157	<0.1			0,430		0,293			0,380	0,387		0,520	0,148		
	D	13	50,2		40,9	44,3	33,3	65,2	53,7		29,5	47,0	47,6		51,0	46,1	44,7		53,5			
246-TCP	A	17	0,179	0,225	0,240	0,283	0,257	<0.1	0,157	0,290	0,393		0,257	0,178	0,190	0,280	0,333	0,443	0,410	0,188	0,191	
	B	16	0,048	0,075	0,083	0,117	0,078	<0.1	0,037	0,101	0,127		0,063	0,058	0,053	0,205	0,097		0,150	0,083	0,066	
	C	14	0,905	1,670	0,441	5,133	0,752	<0.1	0,973	3,600	2,733		1,167			2,000	1,733		3,200	1,274	1,097	
	D	17	59,3		57,4	42,7	48,8	130,0	51,3	32,0	58,6	61,3	57,6	124,0	54,1	70,8	53,7		58,5		33,1	48,8
345-TCP	A	7	0,019				0,060				0,033		0,020			0,013			0,030	0,113		
	B	7	0,017				0,049				0,033		0,017			0,090			0,027	0,037		
	C	7	0,967				1,647				1,867		1,387			3,550			2,467	1,050		
	D	8	17,6			29,3	16,7		17,0		9,1		21,3			16,1			17,0			
2345-TeCP	A	10	0,012		0,021	0,021	0,008				0,020		0,010		0,993	0,010	0,027			0,124		
	B	9	<0.01		0,030	0,015	0,011				0,013		0,020		1,033	0,040	0,027			0,017		
	C	9	0,467		0,183	1,267	0,422				0,890		0,513			0,595	1,100			0,468		
	D	11	22,1		21,8	16,3	16,9		22,7		22,7		21,7		51,5	9,2	19,7		18,5			
2346-TeCP	A	18	1,763	2,605	1,036	1,027	2,047	<0.1	1,363	2,867	1,800	2,130	2,000	1,180		2,550	4,700	4,067	3,700	1,731	4,618	3,157
	B	18	1,497	2,115	0,976	1,667	2,602	<0.1	1,087	2,633	1,633	1,803	1,380	1,130		3,245	3,667	3,567	3,300	1,779	4,303	2,557
	C	19	135,000	250,000	53,370	22,667	200,430	1,233	106,667	281,500	160,000	285,000	242,333	120,667		267,055	376,667	323,333	286,667	107,100	88,327	281,000
	D	16	53,8		46,2	34,3	48,0	112,9	49,7	27,0	50,5	53,3	48,6	77,7		63,0	92,3		58,5		112,8	35,3
2356-TeCP	A	0			<0.001								<0.01			<0.01						
	B	0			<0.001								<0.01			<0.01						
	C	1			<0.001								0,130			<0.01						
	D	3			1,0								0,2			0,1			<0.1			
PCP	A	20	5,667	5,420	2,669	2,067	6,699	0,467	4,770	7,667	6,433	7,840	5,500	9,083	3,333	7,120	10,400	6,400	5,667	2,382	4,389	7,930
	B	20	1,180	0,780	0,910	1,667	1,445	0,267	0,880	1,600	1,567	1,177	0,967	1,510	0,950	1,830	1,867	0,717	1,733	1,228	2,277	2,127
	C	18	212,7		42,13	20,67	1522	17,10	1168	3000	1667	1793	1558	1900		1357	1650	1203	2100	912,0	544,0	1186,0
	D	17	177,7		63,5	88,5	176,9	281,6	216,7	98,3	114,4	199,0	139,8	509,7	222,3	205,7	233,3		160,0		158,9	171,0

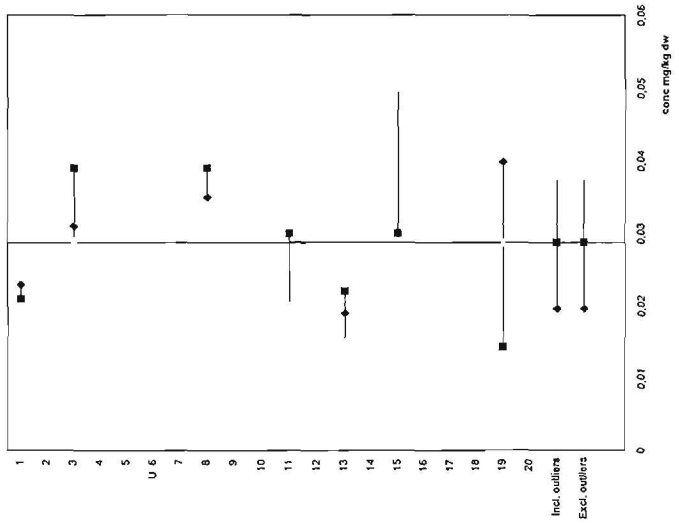
Appendix 3. Line diagrams of chlorophenols analysed from samples A, B and C with the recommended method

2,4-dichlorophenol

Sample A

LAB	1	2	3	n	s(i)	y(i)	Outliers
1	0,023	0,021	0,024	3	0,0015	0,0227	
2							
3	0,031	0,039	0,029	3	0,0053	0,0330	
4							
5							
6	<0.1	<0.1	<0.1	3			U
7							
8	0,035	0,039	0,034	3	0,0026	0,0360	
9							
10							
11	0,03	0,03	0,02	3	0,0058	0,0267	
12							
13	0,019	0,022	0,015	3	0,0035	0,0187	
14							
15	0,03	0,03	0,05	3	0,0115	0,0367	
16							
17							
18							
19	0,0398	0,0143	0,0287	3	0,0128	0,0276	
20							

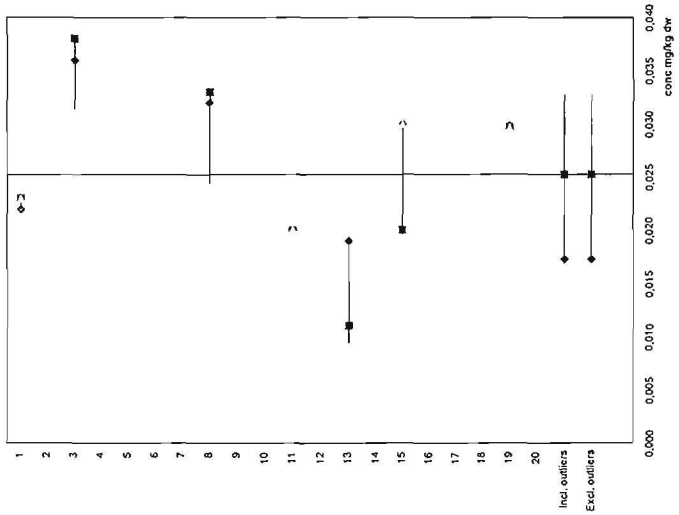
No. of laboratories:	8
No. of laboratories included in the calculations (p):	7
Mean (m):	0,0288
Standard deviation within the laboratories (sr):	0,0074
Standard deviation between the laboratories (sR):	0,0091
Coefficient of laboratories within the laboratories (CVr%):	25,6
Coefficient of laboratories between the laboratories (CVR%):	31,6



Sample B

LAB	1	2	3	n	s(i)	y(i)	Outliers
1	0,022	0,023	0,023	3	0,000577	0,022667	
2							
3	0,036	0,038	0,031	3	0,003606	0,035	
4							
5							
6	<0.1	<0.1	<0.1	3			U
7							
8	0,032	0,033	0,024	3	0,004933	0,029667	
9							
10							
11	0,02	0,02	0,02	3	3,29E-10	0,02	
12							
13	0,019	0,011	0,009	3	0,005292	0,013	
14							
15	0,03	0,02	0,03	3	0,005774	0,026667	
16							
17							
18							
19	0,0298	0,0297	0,0296	3	0,0001	0,0297	
20							

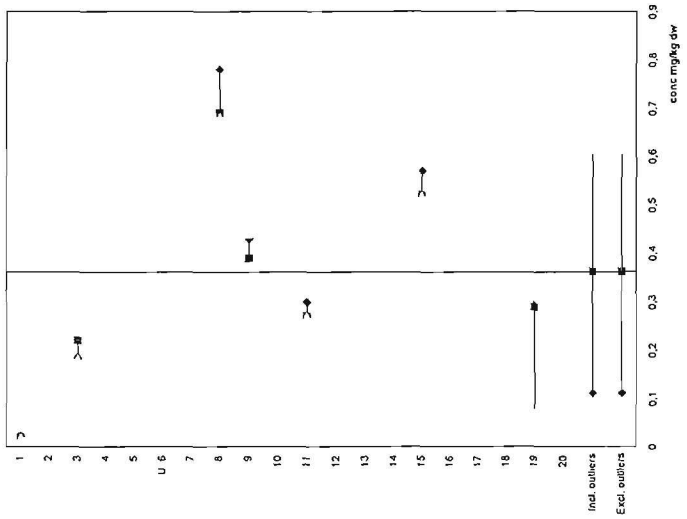
No. of laboratories:	8
No. of laboratories included in the calculations (p):	7
Mean (m):	0,025243
Standard deviation within the laboratories (sr):	0,003761
Standard deviation between the laboratories (sR):	0,007929
Coefficient of laboratories within the laboratories (CVr%):	14,89882
Coefficient of laboratories between the laboratories (CVR%):	31,41253



Sample C

LAB	1	2	3	n	s(i)	y(i)	Outliers
1	0,022	0,02	0,019	3	0,001528	0,020333	
2							
3	0,185	0,22	0,184	3	0,020502	0,196333	
4							
5							
6	<0.1	<0.1	<0.1	3			U
7							
8	0,78	0,69	0,68	3	0,055076	0,716667	
9	0,43	0,39	0,44	3	0,026458	0,42	
10							
11	0,3	0,27	0,27	3	0,017321	0,28	
12							
13							
14							
15	0,57	0,52	0,52	3	0,028868	0,536667	
16							
17							
18							
19	0,2934	0,2883	0,0698	3	0,127649	0,217167	C**
20							

No. of laboratories:	8
No. of laboratories included in the calculations (p):	6
Mean (m):	0,361667
Standard deviation within the laboratories (sr):	0,029691
Standard deviation between the laboratories (sR):	0,250401
Coefficient of laboratories within the laboratories (CVr%):	8,209493
Coefficient of laboratories between the laboratories (CVR%):	69,23541



Explanation of outliers

U	Indicates that the laboratory results are not included in the calculation
C*	Indicates Cochran's straggler
G*	Indicates Grubb's straggler
C**	Indicates Cochran's outlier
G**	Indicates Grubb's outlier

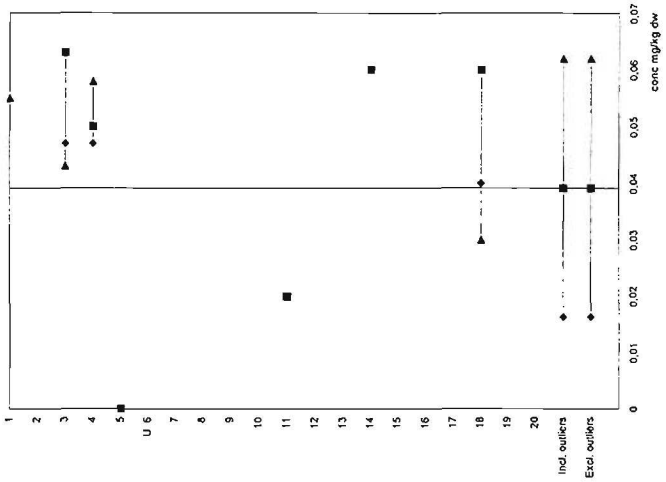
3,4-dichlorophenol

Sample A

LAB	1	2	3	n	s(i)	y(i)	Outliers
1	<0.01	<0.01	0,055	3	0	0,055	
2							
3	0,047	0,063	0,043	3	0,010583	0,051	
4	0,047	0,05	0,058	3	0,005686	0,051667	
5	0	0	0	3	0	0	
6	<0.1	<0.1	<0.1	3			U
7							
8							
9							
10							
11	0,02	0,02	0,02	3	3,29E-10	0,02	
12							
13							
14	0,06	0,06		2	0	0,06	
15							
16							
17							
18	0,04	0,06	0,03	3	0,015275	0,043333	
19							
20							

No. of laboratories: 8
No. of laboratories included in the calculations (p): 7

Mean (m): 0,03915
Standard deviation within the laboratories (sr): 0,007623
Standard deviation between the laboratories (sR): 0,022827
Coefficient of laboratories within the laboratories (CVr%): 19,47
Coefficient of laboratories between the laboratories (CVR%): 58,30594

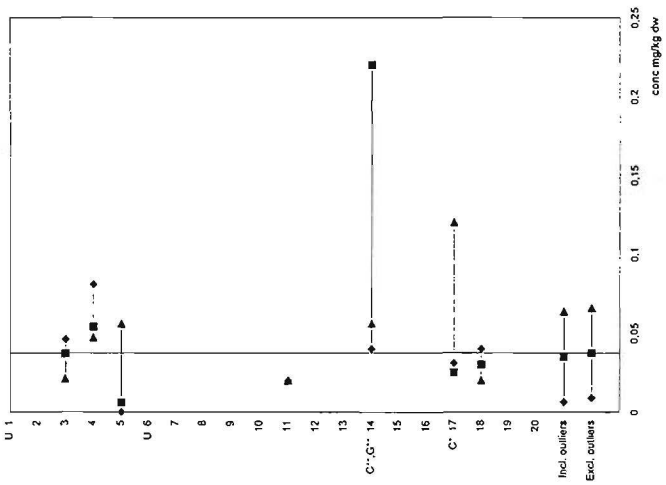


Sample B

LAB	1	2	3	n	s(i)	y(i)	Outliers
1	<0.01	<0.01	<0.01	3			U
2							
3	0,046	0,037	0,021	3	0,012662	0,034667	
4	0,081	0,054	0,047	3	0,017954	0,060667	
5	0	0,006	0,056	3	0,030746	0,020667	
6	<0.1	<0.1	<0.1	3			U
7							
8							
9							
10							
11	0,02	<0.01	0,02	3	0	0,02	
12							
13							
14	0,04	0,22		2	0,127279	0,13	C**,G**
15							
16							
17	0,031	0,025	0,12	3	0,053201	0,058667	C*
18	0,04	0,03	0,02	3	0,01	0,03	
19							
20							

No. of laboratories: 9
No. of laboratories included in the calculations (p): 6

Mean (m): 0,037444
Standard deviation within the laboratories (sr): 0,026952
Standard deviation between the laboratories (sR): 0,028495
Coefficient of laboratories within the laboratories (CVr%): 71,97757
Coefficient of laboratories between the laboratories (CVR%): 76,1

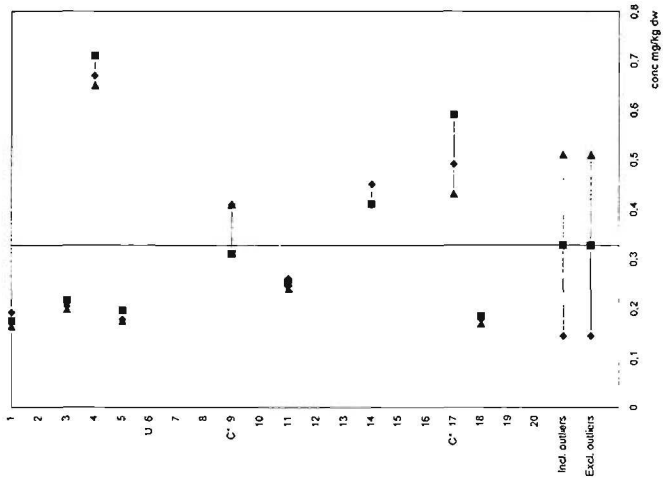


Sample C

LAB	1	2	3	n	s(i)	y(i)	Outliers
1	0,192	0,175	0,164	3	0,014107	0,177	
2							
3	0,204	0,216	0,198	3	0,009165	0,206	
4	0,67	0,71	0,65	3	0,030551	0,676667	
5	0,178	0,196	0,175	3	0,011358	0,183	
6	<0.1	<0.1	<0.1	3			U
7							
8							
9	0,41	0,31	0,41	3	0,057735	0,376667	C*
10							
11	0,26	0,25	0,24	3	0,01	0,25	
12							
13							
14	0,45	0,41	0	2	0,028284	0,43	
15							
16							
17	0,49	0,59	0,43	3	0,080829	0,503333	C*
18	0,177	0,184	0,169	3	0,007506	0,176667	
19							
20							

No. of laboratories: 10
No. of laboratories included in the calculations (p): 9

Mean (m): 0,327231
Standard deviation within the laboratories (sr): 0,037209
Standard deviation between the laboratories (sR): 0,182522
Coefficient of laboratories within the laboratories (CVr%): 11,37087
Coefficient of laboratories between the laboratories (CVR%): 55,77773



Explanation of outliers

U	Indicates that the laboratory results are not included in the calculation
C*	Indicates Cochran's straggler
G*	Indicates Grubb's straggler
C**	Indicates Cochran's outlier
G**	Indicates Grubb's outlier

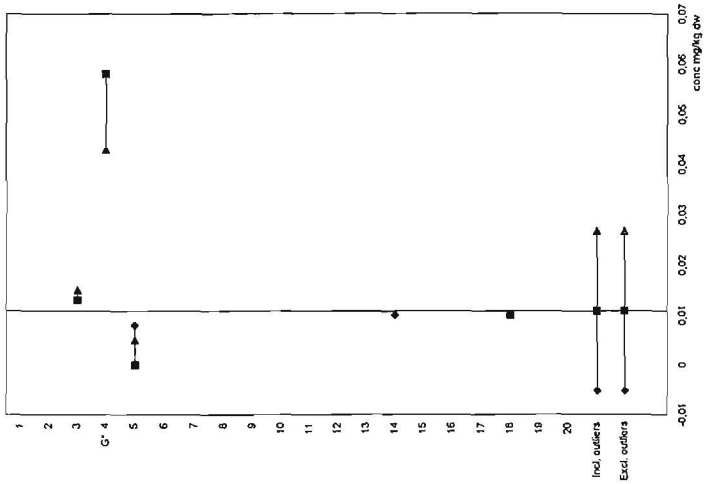
3,5-dichlorophenol

Sample A

LAB	1	2	3	n	s(i)	y(i)	Outliers
1	<0.01	<0.01	<0.01	3			
2							
3	0,013	0,013	0,015	3	0,001155	0,013667	
4		0,058	0,043	2	0,010607	0,0505	G*
5	0,008	0	0,005	3	0,004041	0,004333	
6							
7							
8							
9							
10							
11	<0.01	<0.01	<0.01	3			
12							
13							
14	0,01	<0.01		2	0	0,01	
15							
16							
17							
18	0,01	0,01	0,01	3	1,65E-10	0,01	
19							
20							

No. of laboratories: 7
No. of laboratories included in the calculations (p): 7

Mean (m): 0,010789
Standard deviation within the laboratories (sr): 0,00351
Standard deviation between the laboratories (sR): 0,016964
Coefficient of laboratories within the laboratories (CVr%): 32,53084
Coefficient of laboratories between the laboratories (CVR%): 147,9567

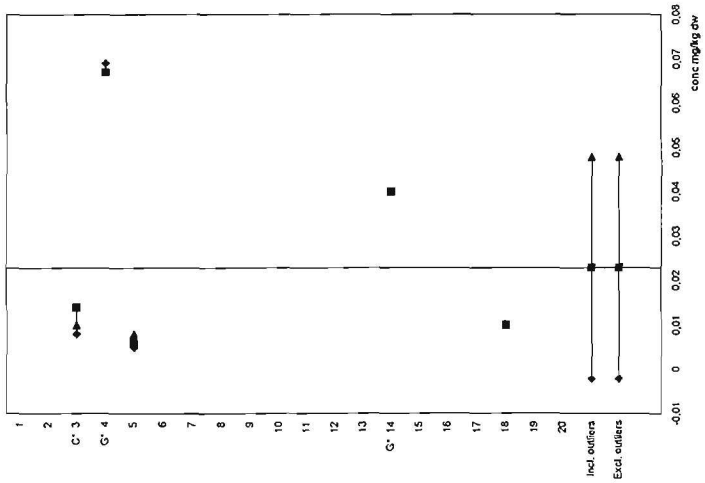


Sample B

LAB	1	2	3	n	s(i)	y(i)	Outliers
1	<0.01	<0.01	<0.01	3			
2							
3	0,008	0,014	0,01	3	0,003055	0,010667	
4	0,069	0,067	0	2	0,001414	0,068	G*
5	0,005	0,006	0,008	3	0,001528	0,006333	
6							
7							
8							
9							
10							
11	<0.01	<0.01	<0.01	3			
12							
13							
14	<0.01	0,04	0	2	0	0,04	G*
15							
16							
17							
18	0,01	0,01	0,01	3	1,65E-10	0,01	
19							
20							

No. of laboratories: 7
No. of laboratories included in the calculations (p): 5

Mean (m): 0,022846
Standard deviation within the laboratories (sr): 0,00178
Standard deviation between the laboratories (sR): 0,025004
Coefficient of laboratories within the laboratories (CVr%): 7,789114
Coefficient of laboratories between the laboratories (CVR%): 109,4448

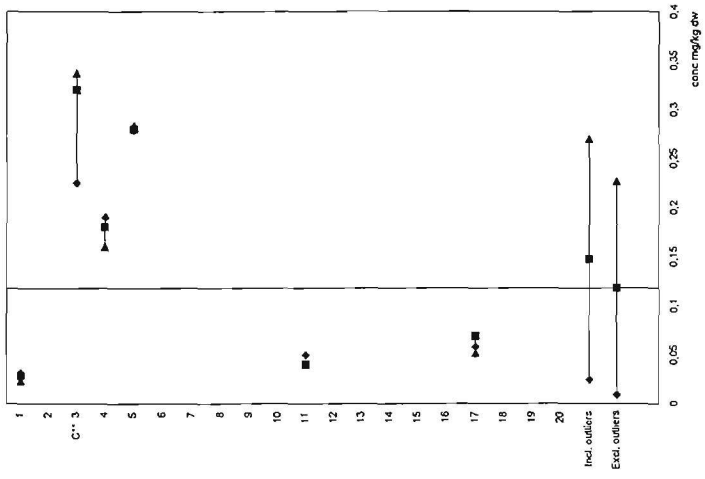


Sample C

LAB	1	2	3	n	s(i)	y(i)	Outliers
1	0,032	0,029	0,024	3	0,004041	0,028333	
2							
3	0,225	0,32	0,337	3	0,060357	0,294	C**
4	0,19	0,18	0,16	3	0,015275	0,176667	
5	0,279	0,28	0,284	3	0,002646	0,281	
6							
7							
8							
9							
10							
11	0,05	0,04	0,04	3	0,005774	0,043333	
12							
13							
14	<0.01	<0.01		2			
15							
16							
17	0,058	0,069	0,052	3	0,008622	0,059667	
18	<0.03	<0.03	<0.03	0			
19							
20							

No. of laboratories: 7
No. of laboratories included in the calculations (p): 5

Mean (m): 0,1178
Standard deviation within the laboratories (sr): 0,008536
Standard deviation between the laboratories (sR): 0,108654
Coefficient of laboratories within the laboratories (CVr%): 7,246348
Coefficient of laboratories between the laboratories (CVR%): 92,23611



Explanation of outliers

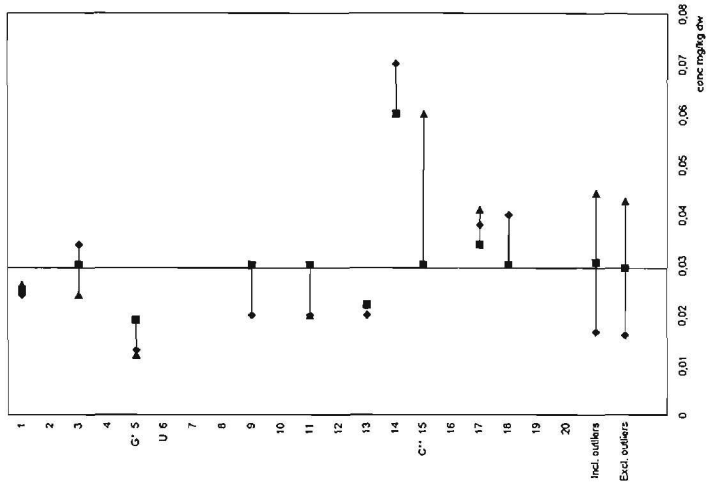
U	Indicates that the laboratory results are not included in the calculation
C*	Indicates Cochran's straggler
G*	Indicates Grubb's straggler
C**	Indicates Cochran's outlier
G**	Indicates Grubb's outlier

2,4,5-trichlorophenol

Sample A

LAB	1	2	3	n	s(i)	y(i)	Outliers
1	0,024	0,025	0,026	3	0,001	0,025	
2							
3	0,034	0,03	0,024	3	0,005033	0,029333	
4	<0.01	<0.01	<0.01	3			
5	0,013	0,019	0,012	3	0,003786	0,014667	G*
6	<0.1	<0.1	<0.1	3			
7							
8							
9	0,02	0,03	0,03	3	0,005774	0,026667	
10							
11	0,02	0,03	0,02	3	0,005774	0,023333	
12							
13	0,02	0,022	0,022	3	0,001155	0,021333	
14	0,07	0,06		2	0,007071	0,065	
15	0,03	0,03	0,06	3	0,017321	0,04	C**
16							
17	0,038	0,034	0,041	3	0,003512	0,037667	
18	0,04	0,03	0,03	3	0,005774	0,033333	
19							
20							

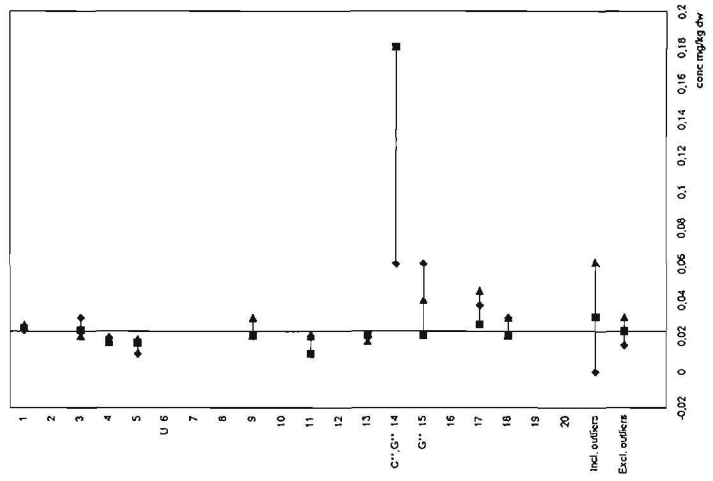
No. of laboratories:	12
No. of laboratories included in the calculations (p):	9
Mean (m):	0,029385
Standard deviation within the laboratories (sr):	0,004593
Standard deviation between the laboratories (sR):	0,013397
Coefficient of laboratories within the laboratories (CVr%):	15,63151
Coefficient of laboratories between the laboratories (CVR%):	45,59047



Sample B

LAB	1	2	3	n	s(i)	y(i)	Outliers
1	0,023	0,024	0,026	3	0,002	0,024	
2							
3	0,03	0,023	0,02	3	0,005	0,024	
4	0,019	0,016	<0.01	3	0,002	0,018	
5	0,01	0,016	0,018	3	0,004	0,015	
6	<0.1	<0.1	<0.1	3			U
7							
8							
9	0,02	0,02	0,03	3	0,006	0,023	
10							
11	0,02	0,01	0,02	3	0,006	0,017	
12							
13	0,02	0,02	0,017	3	0,002	0,019	
14	0,06	0,18		2	0,085	0,120	C**, G**
15	0,06	0,02	0,04	3	0,020	0,040	C**
16							
17	0,037	0,026	0,045	3	0,010	0,036	
18	0,03	0,02	0,03	3	0,006	0,027	
19							
20							

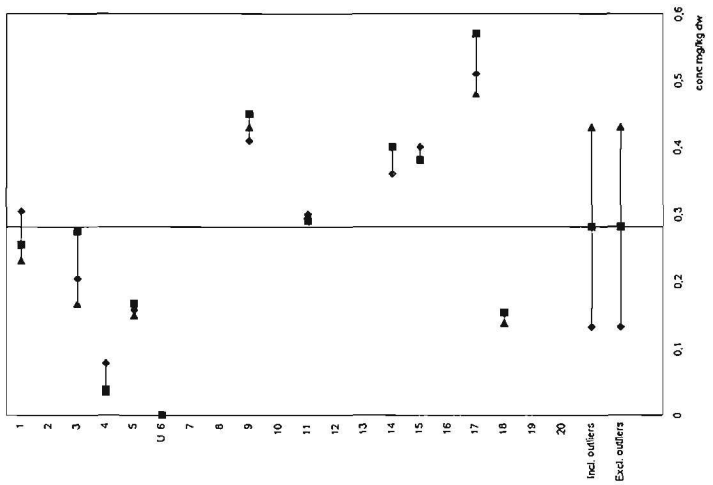
No. of laboratories:	12
No. of laboratories included in the calculations (p):	9
Mean (m):	0,023
Standard deviation within the laboratories (sr):	0,005
Standard deviation between the laboratories (sR):	0,008
Coefficient of laboratories within the laboratories (CVr%):	23,2
Coefficient of laboratories between the laboratories (CVR%):	34,6



Sample C

LAB	1	2	3	n	s(i)	y(i)	Outliers
1	0,304	0,254	0,231	3	0,037323	0,263	
2							
3	0,204	0,274	0,167	3	0,054342	0,215	
4	0,078	0,038	0,035	3	0,024007	0,050	
5	0,157	0,166	0,149	3	0,008505	0,157	
6	<0.1	<0.1	<0.1	3			U
7							
8							
9	0,41	0,45	0,43	3	0,02	0,430	
10							
11	0,3	0,29	0,29	3	0,005774	0,293	
12							
13							
14	0,36	0,4	0	2	0,028284	0,380	
15	0,4	0,38	0,38	3	0,011547	0,387	
16							
17	0,51	0,57	0,48	3	0,045826	0,520	
18	0,152	0,153	0,138	3	0,008386	0,148	
19							
20							

No. of laboratories:	11
No. of laboratories included in the calculations (p):	10
Mean (m):	0,281
Standard deviation within the laboratories (sr):	0,029
Standard deviation between the laboratories (sR):	0,149
Coefficient of laboratories within the laboratories (CVr%):	10,4
Coefficient of laboratories between the laboratories (CVR%):	53,0



Explanation of outliers

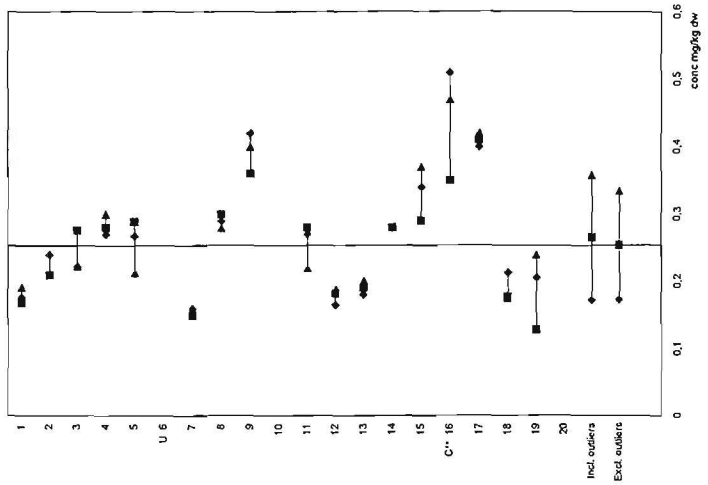
U	Indicates that the laboratory results are not included in the calculation
C*	Indicates Cochran's straggler
G*	Indicates Grubb's straggler
C**	Indicates Cochran's outlier
G**	Indicates Grubb's outlier

2,4,6-trichlorophenol

Sample A

LAB	1	2	3	n	s(i)	y(i)	Outliers
1	0,177	0,169	0,192	3	0,011676	0,179333	
2	0,24	0,21	0	2	0,021213	0,225	
3	0,222	0,276	0,223	3	0,030892	0,240333	
4	0,27	0,28	0,3	3	0,015275	0,283333	
5	0,268	0,289	0,213	3	0,039247	0,256667	
6	<0.1	<0.1	<0.1	3			U
7	0,16	0,15	0,16	3	0,005774	0,156667	
8	0,29	0,3	0,28	3	0,01	0,29	
9	0,42	0,36	0,4	3	0,030551	0,393333	
10							
11	0,27	0,28	0,22	3	0,032146	0,256667	
12	0,165	0,182	0,188	3	0,011193	0,178333	
13	0,18	0,19	0,2	3	0,01	0,19	
14	0,28	0,28	0	2	0	0,28	
15	0,34	0,29	0,37	3	0,040415	0,333333	
16	0,51	0,35	0,47	3	0,083267	0,443333	C**
17	0,4	0,41	0,42	3	0,01	0,41	
18	0,213	0,177	0,175	3	0,021385	0,188333	
19	0,2053	0,1279	0,2389	3	0,056922	0,1907	
20							

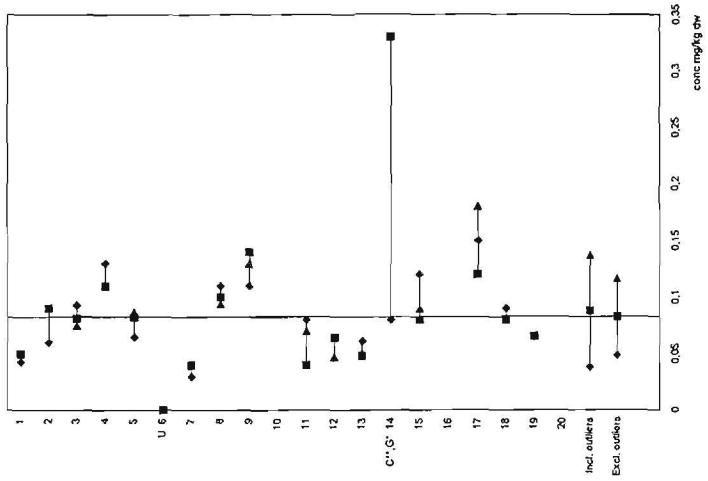
No. of laboratories:	18
No. of laboratories included in the calculations (p):	16
Mean (m):	0,253285
Standard deviation within the laboratories (sr):	0,02691
Standard deviation between the laboratories (sR):	0,080631
Coefficient of laboratories within the laboratories (CVr%):	10,62452
Coefficient of laboratories between the laboratories (CVR%):	31,83397



Sample B

LAB	1	2	3	n	s(i)	y(i)	Outliers
1	0,043	0,05	0,05	3	0,004041	0,047667	
2	0,06	0,09		2	0,021213	0,075	
3	0,093	0,081	0,075	3	0,009165	0,083	
4	0,13	0,11	0,11	3	0,011547	0,116667	
5	0,065	0,082	0,087	3	0,011533	0,078	
6	<0.1	<0.1	<0.1	3			U
7	0,03	0,04	0,04	3	0,005774	0,036667	
8	0,11	0,1	0,094	3	0,008083	0,101333	
9	0,11	0,14	0,13	3	0,015275	0,126667	
10							
11	0,08	0,04	0,07	3	0,020817	0,063333	
12	0,064	0,064	0,047	3	0,009815	0,058333	
13	0,061	0,048	0,05	3	0,007	0,053	
14	0,08	0,33		2	0,176777	0,205	C**, G*
15	0,12	0,08	0,09	3	0,020817	0,096667	
16							
17	0,15	0,12	0,18	3	0,03	0,15	
18	0,09	0,08	0,08	3	0,005774	0,083333	
19	0,0655	0,0656	0,0656	3	5,77E-05	0,065567	
20							

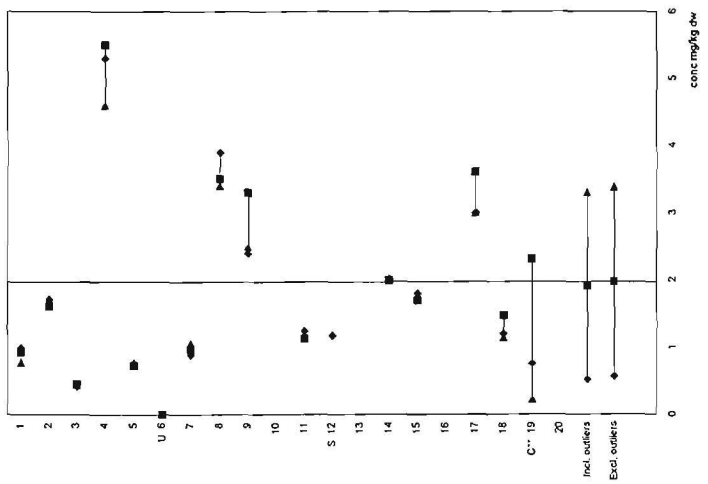
No. of laboratories:	17
No. of laboratories included in the calculations (p):	15
Mean (m):	0,082516
Standard deviation within the laboratories (sr):	0,014066
Standard deviation between the laboratories (sR):	0,033653
Coefficient of laboratories within the laboratories (CVr%):	17,04684
Coefficient of laboratories between the laboratories (CVR%):	40,7831



Sample C

LAB	1	2	3	n	s(i)	y(i)	Outliers
1	1,003	0,933	0,779	3	0,114595	0,905	
2	1,72	1,62		2	0,070711	1,67	
3	0,421	0,455	0,447	3	0,017776	0,441	
4	5,3	5,5	4,6	3	0,472582	5,133333	
5	0,76	0,728	0,767	3	0,020793	0,751667	
6	<0.1	<0.1	<0.1	3			U
7	0,89	0,97	1,06	3	0,085049	0,973333	
8	3,9	3,5	3,4	3	0,264575	3,6	
9	2,4	3,3	2,5	3	0,493288	2,733333	
10							
11	1,24	1,13	1,13	3	0,063509	1,166667	
12	1,18			1			U
13							
14	2,01	1,99		2	0,014142	2	
15	1,8	1,7	1,7	3	0,057735	1,733333	
16							
17	3	3,6	3	3	0,34641	3,2	
18	1,202	1,47	1,151	3	0,17136	1,274333	
19	0,7578	2,3092	0,2249	3	1,08283	1,0973	C**
20							

No. of laboratories:	16
No. of laboratories included in the calculations (p):	13
Mean (m):	1,975027
Standard deviation within the laboratories (sr):	0,244457
Standard deviation between the laboratories (sR):	1,40348
Coefficient of laboratories within the laboratories (CVr%):	12,37741
Coefficient of laboratories between the laboratories (CVR%):	71,06131



Explanation of outliers

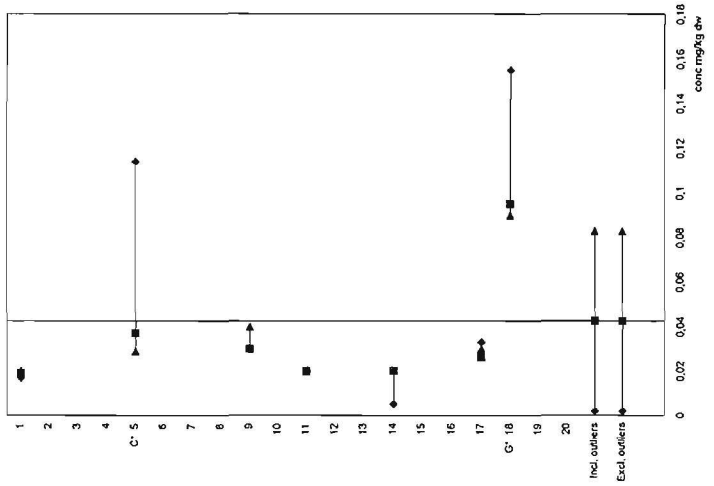
U	Indicates that the laboratory results are not included in the calculation
C*	Indicates Cochran's straggler
G*	Indicates Grubb's straggler
C**	Indicates Cochran's outlier
G**	Indicates Grubb's outlier

3,4,5-trichlorophenol

Sample A

LAB	1	2	3	n	s(i)	y(i)	Outliers
1	0,017	0,019	0,02	3	0,001528	0,018667	
2							
3							
4							
5	0,114	0,037	0,029	3	0,046936	0,06	C*
6							
7							
8							
9	0,03	0,03	0,04	3	0,005774	0,033333	
10							
11	0,02	0,02	0,02	3	3,29E-10	0,02	
12							
13							
14	0,005	0,02		2	0,010607	0,0125	
15							
16							
17	0,033	0,026	0,03	3	0,003512	0,029667	
18	0,155	0,095	0,09	3	0,036171	0,113333	G*
19							
20							

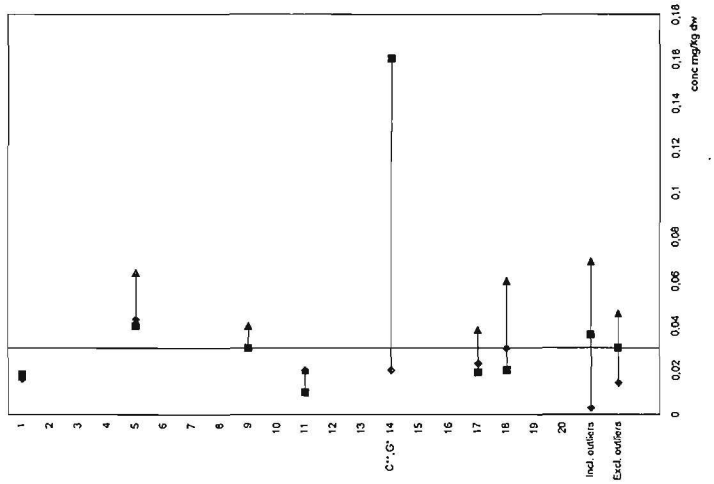
No. of laboratories:	7
No. of laboratories included in the calculations (p):	7
Mean (m):	0,0425
Standard deviation within the laboratories (sr):	0,023585
Standard deviation between the laboratories (sR):	0,040403
Coefficient of laboratories within the laboratories (CVr%):	55,49369
Coefficient of laboratories between the laboratories (CVR%):	95,06598



Sample B

LAB	1	2	3	n	s(i)	y(i)	Outliers
1	0,016	0,018	0,017	3	0,001	0,017	
2							
3							
4							
5	0,043	0,04	0,064	3	0,013077	0,049	
6							
7							
8							
9	0,03	0,03	0,04	3	0,005774	0,033333	
10							
11	0,02	0,01	0,02	3	0,005774	0,016667	
12							
13							
14	0,02	0,16		2	0,098995	0,09	C**, G*
15							
16							
17	0,023	0,019	0,038	3	0,010017	0,026667	
18	0,03	0,02	0,06	3	0,020817	0,036667	
19							
20							

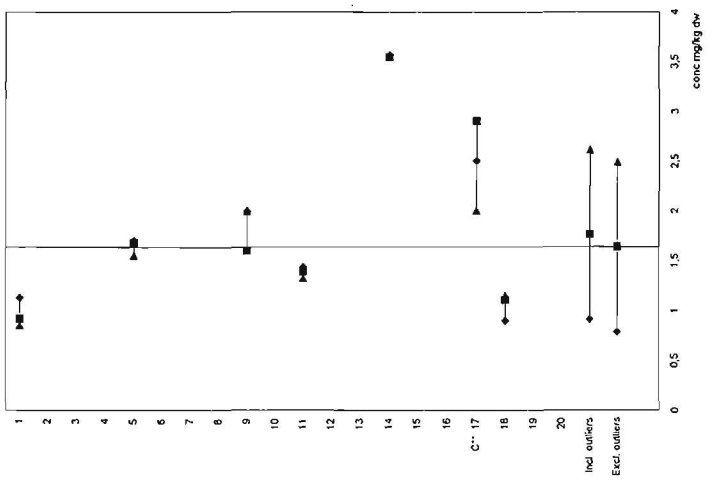
No. of laboratories:	7
No. of laboratories included in the calculations (p):	6
Mean (m):	0,029889
Standard deviation within the laboratories (sr):	0,011346
Standard deviation between the laboratories (sR):	0,015514
Coefficient of laboratories within the laboratories (CVr%):	37,9592
Coefficient of laboratories between the laboratories (CVR%):	51,90608



Sample C

LAB	1	2	3	n	s(i)	y(i)	Outliers
1	1,13	0,917	0,855	3	0,144244	0,967333	
2							
3							
4							
5	1,7	1,683	1,557	3	0,078117	1,646667	
6							
7							
8							
9	2	1,6	2	3	0,23094	1,866667	
10							
11	1,44	1,39	1,33	3	0,055076	1,386667	
12							
13							
14	3,56	3,54	0	2	0,014142	3,55	
15							
16							
17	2,5	2,9	2	3	0,450925	2,466667	C**
18	0,898	1,105	1,147	3	0,1333	1,05	
19							
20							

No. of laboratories:	7
No. of laboratories included in the calculations (p):	6
Mean (m):	1,638353
Standard deviation within the laboratories (sr):	0,135609
Standard deviation between the laboratories (sR):	0,850515
Coefficient of laboratories within the laboratories (CVr%):	8,277172
Coefficient of laboratories between the laboratories (CVR%):	51,91282



Explanation of outliers

U	Indicates that the laboratory results are not included in the calculation
C*	Indicates Cochran's straggler
G*	Indicates Grubb's straggler
C**	Indicates Cochran's outlier
G**	Indicates Grubb's outlier

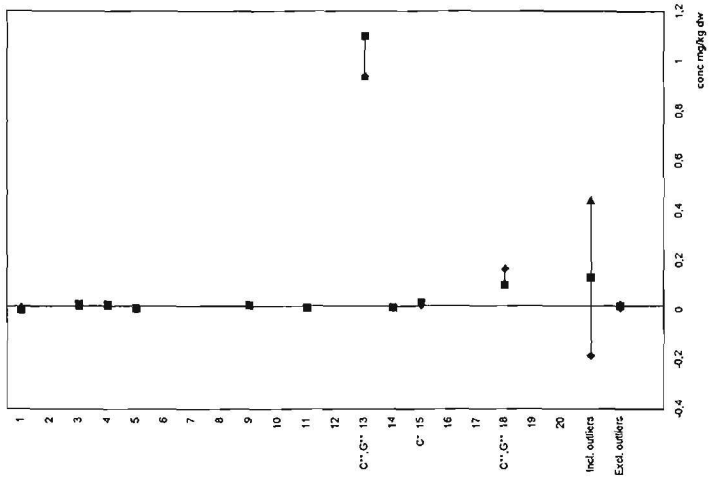
2,3,4,5-tetrachlorophenol

Sample A

LAB	1	2	3	n	s(i)	y(i)	Outliers
1	0,011	<0.01	0,013	3	0,001414	0,012	
2							
3	0,022	0,024	0,018	3	0,003055	0,021333	
4	0,022	0,023	0,018	3	0,002646	0,021	
5	0,006	0,007	0,01	3	0,002082	0,007667	
6							
7							
8							
9	0,02	0,02	0,02	3	3,29E-10	0,02	
10							
11	0,01	0,01	0,01	3	1,65E-10	0,01	
12							
13	0,94	1,1	0,94	3	0,092376	0,993333	C**, G**
14	0,01	0,01		2	0	0,01	
15	0,02	0,03	0,03	3	0,005774	0,026667	C*
16							
17							
18	0,166	0,099	0,108	3	0,036364	0,124333	C**, G**
19							
20							

No. of laboratories: 10
No. of laboratories included in the calculations (p): 8

Mean (m): 0,0148
Standard deviation within the laboratories (sr): 0,001944
Standard deviation between the laboratories (sR): 0,006184
Coefficient of laboratories within the laboratories (CVr%): 13,13277
Coefficient of laboratories between the laboratories (CVR%): 41,78655

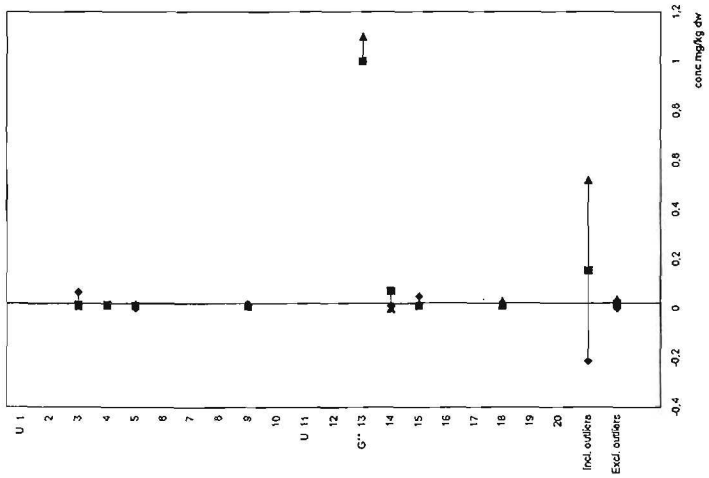


Sample B

LAB	1	2	3	n	s(i)	y(i)	Outliers
1	<0.01	<0.01	<0.01	3			
2							
3	0,066	0,015	0,01	3	0,030989	0,030333	
4	0,015	0,015	0,014	3	0,000577	0,014667	
5	0,003	0,011	0,018	3	0,007506	0,010667	
6							
7							
8							
9	0,02	0,01	0,01	3	0,005774	0,013333	
10							
11	<0.01	<0.01	0,02	3	0	0,02	
12							
13	1	1	1,1	3	0,057735	1,033333	G**
14	0,01	0,07		2	0,042426	0,04	
15	0,05	0,01	0,02	3	0,020817	0,026667	
16							
17							
18	0,01	0,01	0,03	3	0,011547	0,016667	
19							
20							

No. of laboratories: 10
No. of laboratories included in the calculations (p): 7

Mean (m): 0,02085
Standard deviation within the laboratories (sr): 0,019678
Standard deviation between the laboratories (sR): 0,018811
Coefficient of laboratories within the laboratories (CVr%): 94,37976
Coefficient of laboratories between the laboratories (CVR%): 90,21997

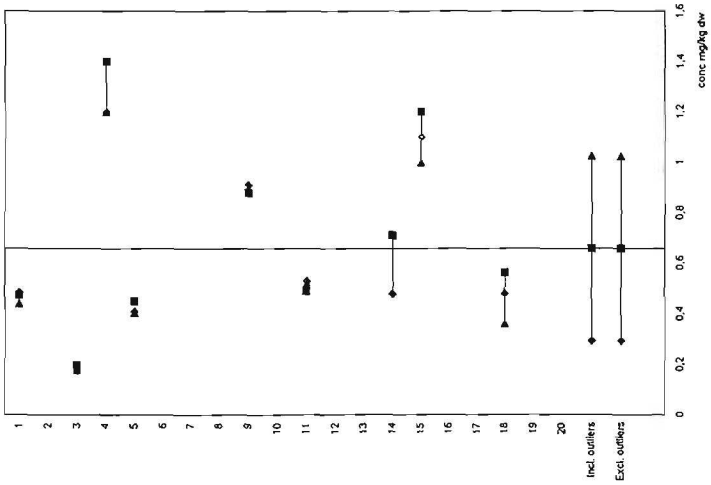


Sample C

LAB	1	2	3	n	s(i)	y(i)	Outliers
1	0,485	0,474	0,441	3	0,022898	0,466667	
2							
3	0,176	0,196	0,177	3	0,011269	0,183	
4	1,2	1,4	1,2	3	0,11547	1,266667	
5	0,411	0,45	0,406	3	0,02409	0,422333	
6							
7							
8							
9	0,91	0,88	0,88	3	0,017321	0,89	
10							
11	0,53	0,49	0,52	3	0,020817	0,513333	
12							
13							
14	0,48	0,71		2	0,162635	0,595	
15	1,1	1,2	1	3	0,1	1,1	
16							
17							
18	0,479	0,562	0,362	3	0,100481	0,467667	
19							
20							

No. of laboratories: 9
No. of laboratories included in the calculations (p): 9

Mean (m): 0,658423
Standard deviation within the laboratories (sr): 0,07563
Standard deviation between the laboratories (sR): 0,365209
Coefficient of laboratories within the laboratories (CVr%): 11,4866
Coefficient of laboratories between the laboratories (CVR%): 55,46722



Explanation of outliers

U	Indicates that the laboratory results are not included in the calculation
C*	Indicates Cochran's straggler
G*	Indicates Grubb's straggler
C**	Indicates Cochran's outlier
G**	Indicates Grubb's outlier

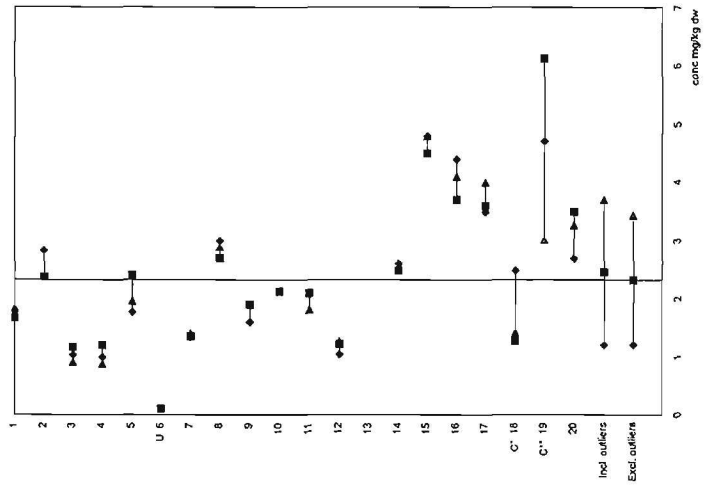
2,3,4,6-tetrachlorophenol

Sample A

LAB	1	2	3	n	s(i)	y(i)	Outliers
1	1,78	1,67	1,84	3	0,086217	1,763333	
2	2,83	2,38		2	0,318198	2,605	
3	1,034	1,165	0,908	3	0,128508	1,035667	
4	1	1,2	0,88	3	0,161658	1,026667	
5	1,773	2,406	1,963	3	0,324817	2,047333	
6	0,1	0,1	<0.1	3			U
7	1,34	1,35	1,4	3	0,032146	1,363333	
8	3	2,7	2,9	3	0,152753	2,866667	
9	1,6	1,9	1,9	3	0,173205	1,8	
10	2,13	2,13	2,13	3	0	2,13	
11	2,08	2,1	1,82	3	0,156205	2	
12	1,05	1,22	1,27	3	0,115326	1,18	
13							
14	2,61	2,49		2	0,084853	2,55	
15	4,8	4,5	4,8	3	0,173205	4,7	
16	4,4	3,7	4,1	3	0,351188	4,066667	
17	3,5	3,6	4	3	0,264575	3,7	
18	2,491	1,275	1,426	3	0,662782	1,730667	C*
19	4,7088	6,1264	3,0182	3	1,556097	4,6178	C**
20	2,7	3,5	3,27	3	0,411866	3,156667	

No. of laboratories: 19
No. of laboratories included in the calculations (p): 17

Mean (m): 2,326755
Standard deviation within the laboratories (sr): 0,266238
Standard deviation between the laboratories (sR): 1,114965
Coefficient of laboratories within the laboratories (CVr%): 11,44248
Coefficient of laboratories between the laboratories (CVR%): 47,9193

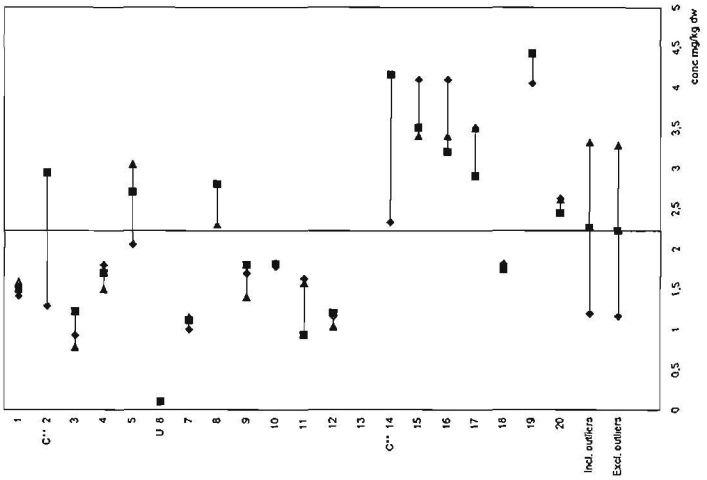


Sample B

LAB	1	2	3	n	s(i)	y(i)	Outliers
1	1,41	1,49	1,59	3	0,090185	1,496667	
2	1,29	2,94		2	1,166726	2,115	C**
3	0,927	1,22	0,78	3	0,224001	0,975667	
4	1,8	1,7	1,5	3	0,152753	1,666667	
5	2,056	2,702	3,049	3	0,503947	2,602333	
6	<0.1	0,1	<0.1	3			U
7	1	1,11	1,15	3	0,077675	1,086667	
8	2,8	2,8	2,3	3	0,288675	2,633333	
9	1,7	1,8	1,4	3	0,208167	1,633333	
10	1,78	1,81	1,82	3	0,020817	1,803333	
11	1,63	0,93	1,58	3	0,390512	1,38	
12	1,16	1,2	1,03	3	0,088882	1,13	
13							
14	2,33	4,16		2	1,294005	3,245	C**
15	4,1	3,5	3,4	3	0,378594	3,666667	
16	4,1	3,2	3,4	3	0,472582	3,566667	
17	3,5	2,9	3,5	3	0,34641	3,3	
18	1,811	1,739	1,786	3	0,036556	1,778667	
19	4,0578	4,4257	4,4257	3	0,212407	4,303067	
20	2,62	2,44	2,61	3	0,10116	2,556667	

No. of laboratories: 19
No. of laboratories included in the calculations (p): 16

Mean (m): 2,223733
Standard deviation within the laboratories (sr): 0,270704
Standard deviation between the laboratories (sR): 1,059665
Coefficient of laboratories within the laboratories (CVr%): 12,17341
Coefficient of laboratories between the laboratories (CVR%): 47,6525

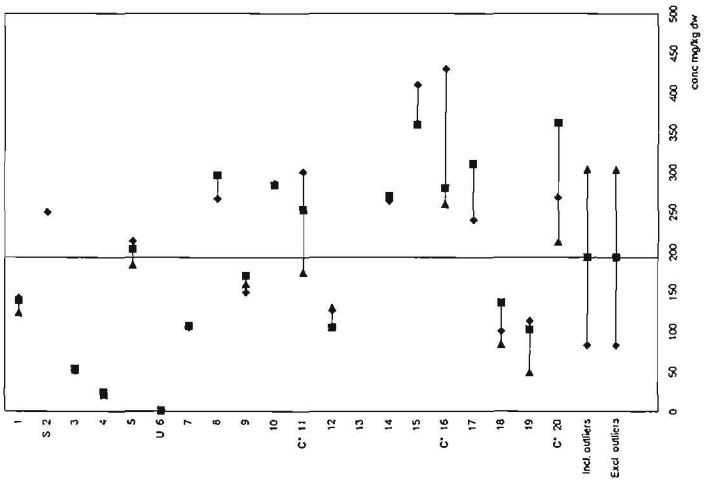


Sample C

LAB	1	2	3	n	s(i)	y(i)	Outliers
1	142	139	124	3	9,643651	135	
2	250			1			U
3	54,16	53,9	52,05	3	1,150522	53,37	
4	23	24	21	3	1,527525	22,66667	
5	213,71	203,74	183,84	3	15,20761	200,43	
6	1,3	1,2	1,2	3			U
7	106	107	107	3	0,57735	106,6667	
8	267	296		2	20,5061	281,5	
9	150	170	160	3	10	160	
10	285	284	286	3	1	285	
11	300	253	174	3	63,67365	242,3333	C*
12	127	105	130	3	13,6504	120,6667	
13							
14	264,26	269,85		2	3,952727	267,055	
15	410	360	360	3	28,86751	376,6667	
16	430	280	260	3	92,91573	323,3333	C*
17	240	310	310	3	40,41452	286,6667	
18	101	136	84,3	3	26,38428	107,1	
19	113,3561	102,4331	49,191	3	34,32976	88,32673	
20	268	362	213	3	75,34587	281	C*

No. of laboratories: 19
No. of laboratories included in the calculations (p): 17

Mean (m): 193,159
Standard deviation within the laboratories (sr): 38,35659
Standard deviation between the laboratories (sR): 109,9827
Coefficient of laboratories within the laboratories (CVr%): 19,85753
Coefficient of laboratories between the laboratories (CVR%): 56,93893



Explanation of outliers

U	Indicates that the laboratory results are not included in the calculation
C*	Indicates Cochran's straggler
G*	Indicates Grubb's straggler
C**	Indicates Cochran's outlier
G**	Indicates Grubb's outlier

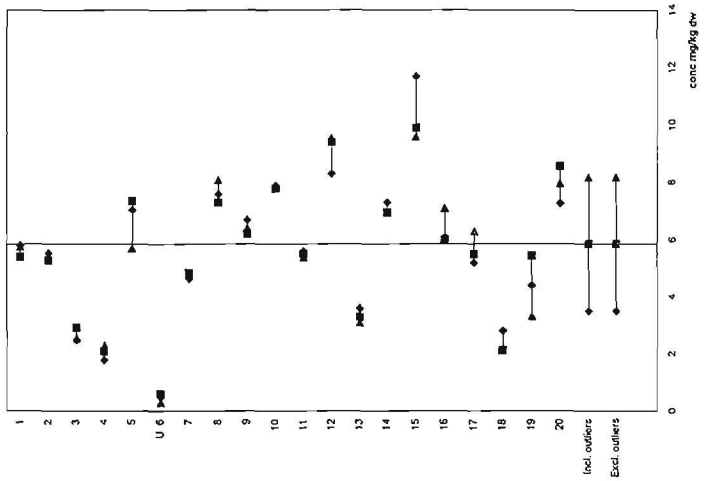
Pentachlorophenol

Sample A

LAB	1	2	3	n	s(i)	y(i)	Outliers
1	5,82	5,41	5,77	3	0,223681	5,666667	
2	5,54	5,3	0	2	0,169706	5,42	
3	2,508	2,933	2,566	3	0,230463	2,669	
4	1,8	2,1	2,3	3	0,251661	2,066667	
5	7,046	7,355	5,696	3	0,882257	6,699	
6	0,5	0,6	0,3	3			U
7	4,64	4,84	4,83	3	0,112694	4,77	
8	7,6	7,3	8,1	3	0,404145	7,666667	
9	6,7	6,2	6,4	3	0,251661	6,433333	
10	7,89	7,79	7,84	3	0,05	7,84	
11	5,6	5,51	5,39	3	0,105357	5,5	
12	8,31	9,4	9,54	3	0,673375	9,083333	
13	3,6	3,3	3,1	3	0,251661	3,333333	
14	7,3	6,94	0	2	0,254558	7,12	
15	11,7	9,9	9,6	3	1,135782	10,4	
16	6,1	6	7,1	3	0,608276	6,4	
17	5,2	5,5	6,3	3	0,568624	5,666667	
18	2,823	2,133	2,191	3	0,382729	2,382333	
19	4,3983	5,4349	3,333	3	1,050983	4,388733	
20	7,27	8,56	7,96	3	0,645523	7,93	

No. of laboratories: 20
No. of laboratories included in the calculations (p): 19

Mean (m): 5,850313
Standard deviation within the laboratories (sr): 0,548355
Standard deviation between the laboratories (sR): 2,339507
Coefficient of laboratories within the laboratories (CVr%): 9,373081
Coefficient of laboratories between the laboratories (CVR%): 39,98943

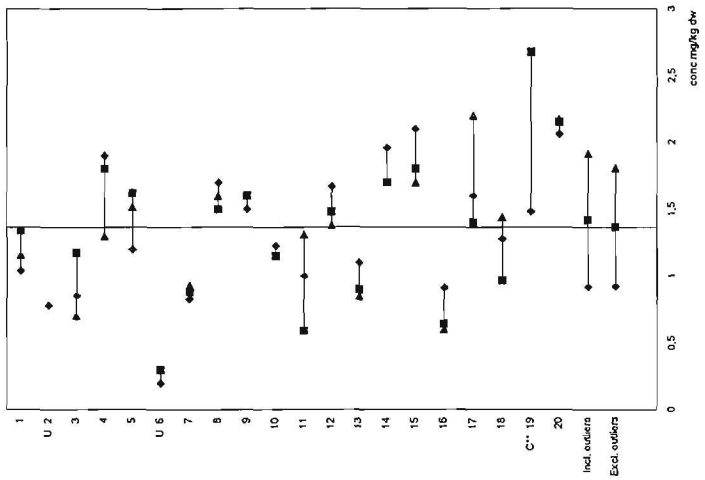


Sample B

LAB	1	2	3	n	s(i)	y(i)	Outliers
1	1,04	1,34	1,16	3	0,150997	1,18	
2	0,78			1			U
3	0,853	1,174	0,704	3	0,240188	0,910333	
4	1,9	1,8	1,3	3	0,321455	1,666667	
5	1,201	1,62	1,515	3	0,218015	1,445333	
6	0,2	0,3	0,3	3			U
7	0,83	0,88	0,93	3	0,05	0,88	
8	1,7	1,5	1,6	3	0,1	1,6	
9	1,5	1,6	1,6	3	0,057735	1,566667	
10	1,23	1,15	1,15	3	0,046188	1,176667	
11	1	0,59	1,31	3	0,361156	0,966667	
12	1,67	1,48	1,38	3	0,147309	1,51	
13	1,1	0,9	0,85	3	0,132288	0,95	
14	1,96	1,7		2	0,183848	1,83	
15	2,1	1,8	1,7	3	0,208167	1,866667	
16	0,91	0,64	0,6	3	0,168622	0,716667	
17	1,6	1,4	2,2	3	0,416333	1,733333	
18	1,278	0,966	1,439	3	0,240484	1,227667	
19	1,4822	2,6748	2,6748	3	0,688548	2,277267	C**
20	2,06	2,15	2,17	3	0,058595	2,126667	

No. of laboratories: 20
No. of laboratories included in the calculations (p): 17

Mean (m): 1,3646
Standard deviation within the laboratories (sr): 0,212092
Standard deviation between the laboratories (sR): 0,44271
Coefficient of laboratories within the laboratories (CVr%): 15,54243
Coefficient of laboratories between the laboratories (CVR%): 32,44246

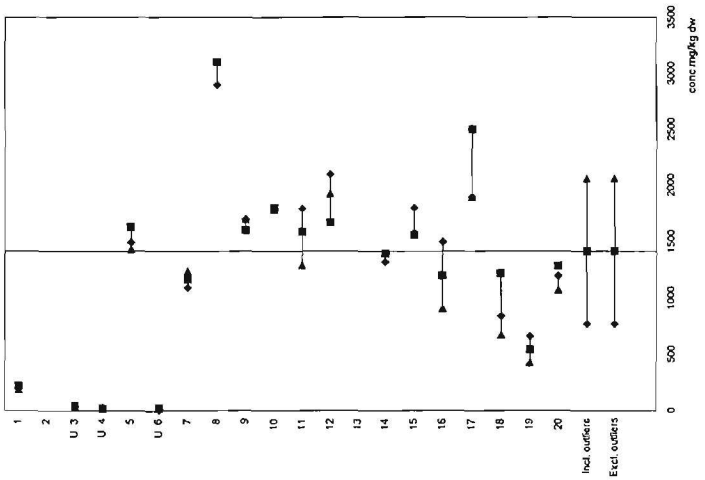


Sample C

LAB	1	2	3	n	s(i)	y(i)	Outliers
1	224	221	193	3	17,09776	212,6667	
2							
3	39,78	44,29	42,32	3			U
4	27	18	17	3			U
5	1497	1631	1437	3	99,32438	1521,667	
6	8,1	19,6	23,6	3			U
7	1097	1168	1238	3	70,50059	1167,667	
8	2900	3100		2	141,4214	3000	
9	1700	1600	1700	3	57,73503	1666,667	
10	1790	1800	1790	3	5,773503	1793,333	
11	1794	1587	1294	3	251,2296	1558,333	
12	2100	1670	1930	3	216,5641	1900	
13							
14	1321,29	1393,39		2	50,9824	1357,34	
15	1800	1560	1590	3	130,767	1650	
16	1500	1200	910	3	295,0141	1203,333	
17	1900	2500	1900	3	346,4102	2100	
18	844	1218	674	3	278,302	912	
19	662,8907	540,2896	428,8887	3	117,0457	544,023	
20	1198	1286	1074	3	106,5082	1186	

No. of laboratories: 18
No. of laboratories included in the calculations (p): 15

Mean (m): 1417,715
Standard deviation within the laboratories (sr): 182,5298
Standard deviation between the laboratories (sR): 646,1887
Coefficient of laboratories within the laboratories (CVr%): 12,87493
Coefficient of laboratories between the laboratories (CVR%): 45,57958



Explanation of outliers

U	Indicates that the laboratory results are not included in the calculation
C*	Indicates Cochran's straggler
G*	Indicates Grubb's straggler
C**	Indicates Cochran's outlier
G**	Indicates Grubb's outlier

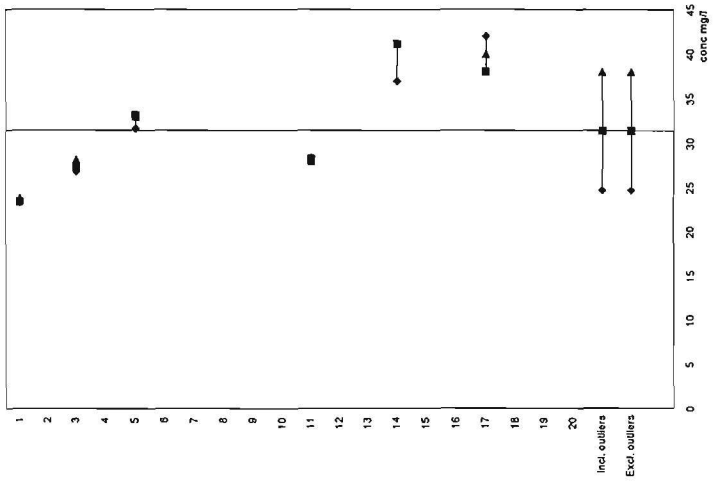
Appendix 4. Line diagrams of chlorophenols analysed from sample D with the recommended method

23-DCP

LAB	1	2	3	n	s(i)	y(i)	Outliers
1	23,3	23,35	23,75	3	0,247	23,47	
2							
3	26,79	27,31	28,13	3	0,676	27,41	
4							
5	31,65	33,15	33,02	3	0,831	32,61	
6							
7							
8							
9							
10							
11	28,4	28,2	28	3	0,2	28,2	
12							
13							
14	37	41,1		2	2,899	39,05	
15							
16							
17	42	38	40	3	2	40	
18							
19							
20							

No. of laboratories: 6
No. of laboratories included in the calculations (p): 6

Mean (m): 31,362
Standard deviation within the laboratories (sr): 1,311
Standard deviation between the laboratories (sR): 6,660
Coefficient of laboratories within the laboratories (CVr%): 4,2
Coefficient of laboratories between the laboratories (CVR%): 21,2

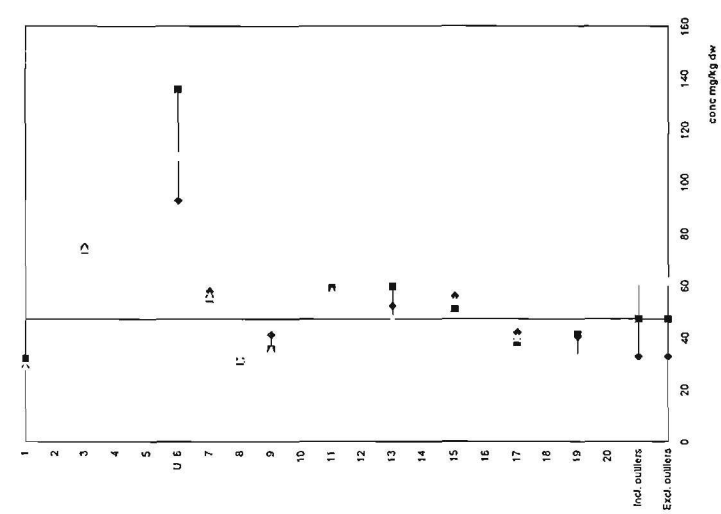


24-DCP

LAB	1	2	3	n	s(i)	y(i)	Outliers
1	28,6	32	28,96	3	1,868	29,85	
2	0	0	0	0	0		
3	75,03	73,75	74,34	3	0,641	74,37	
4							
5							
6	92,9	135,6	109,9	3			U
7	58	55	56	3	1,528	56,33	
8	31	31	32	3	0,577	31,33	
9	41,3	35,5	35,3	3	3,408	37,37	
10							
11	59,3	59,1	57,6	3	0,929	58,67	
12							
13	52,3	59,7	47	3	6,379	53,00	
14							
15	56	51	54	3	2,517	53,67	
16							
17	42	38	40	3	2	40,00	
18							
19	40,362	41,187	31,95	3	5,111	37,83	
20							

No. of laboratories: 12
No. of laboratories included in the calculations (p): 10

Mean (m): 47,24263
Standard deviation within the laboratories (sr): 3,101501
Standard deviation between the laboratories (sR): 14,43522
Coefficient of laboratories within the laboratories (CVr%): 6,6
Coefficient of laboratories between the laboratories (CVR%): 30,6

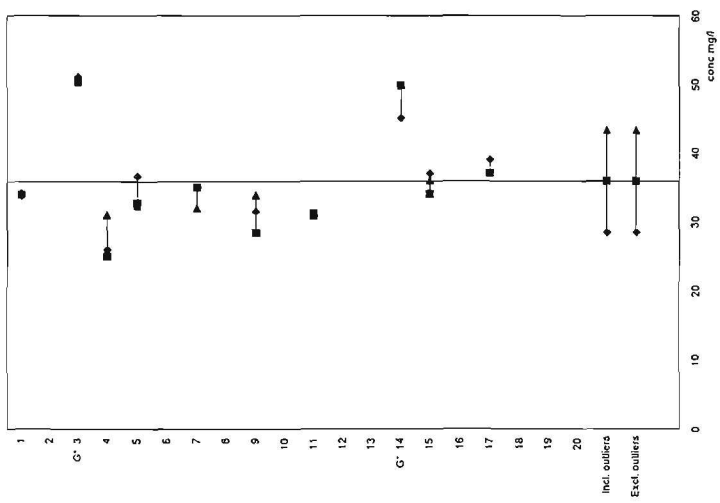


26-DCP

LAB	1	2	3	n	s(i)	y(i)	Outliers
1	33,8	33,95	34,15	3	0,175594	33,96667	
2							
3	51,11	50,47	50,36	3	0,40501	50,64667	G*
4	26	25	31	3	3,21455	27,33333	
5	36,66	32,73	32,37	3	2,379727	33,92	
6							
7	35	35	32	3	1,732051	34	
8							
9	31,5	28,4	33,9	3	2,757414	31,26667	
10							
11	30,9	31,2	30,9	3	0,173205	31	
12							
13							
14	45,1	49,8	0	2	3,323402	47,45	G*
15	37	34	36	3	1,527525	35,66667	
16							
17	39	37	0	2	1,414214	38	
18							
19							
20							

No. of laboratories: 10
No. of laboratories included in the calculations (p): 10

Mean (m): 35,86786
Standard deviation within the laboratories (sr): 1,991104
Standard deviation between the laboratories (sR): 7,415379
Coefficient of laboratories within the laboratories (CVr%): 5,551222
Coefficient of laboratories between the laboratories (CVR%): 20,67416



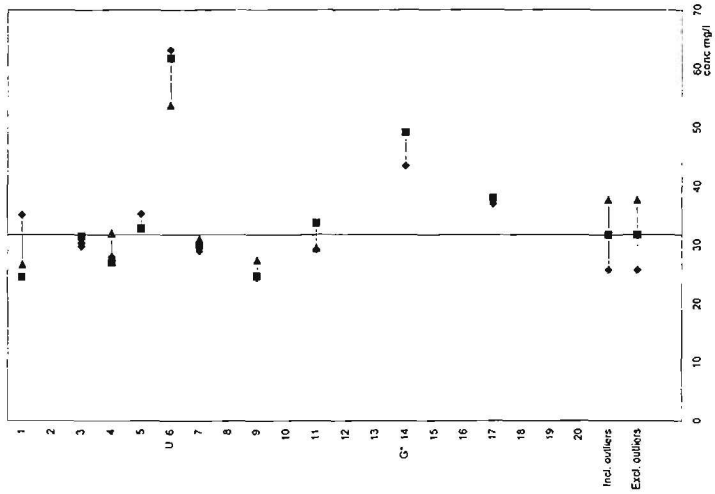
Explanation of outliers

U	Indicates that the laboratory results are not included in the calculation
C*	Indicates Cochran's straggler
G*	Indicates Grubb's straggler
C**	Indicates Cochran's outlier
G**	Indicates Grubb's outlier

34-DCP

LAB	1	2	3	n	s(i)	y(i)	Outliers
1	35,15	24,55	26,7	3	5,603347	28,8	
2							
3	29,81	31,54	30,89	3	0,873861	30,74667	
4	28	27	32	3	2,645751	29	
5	35,35	32,84	32,88	3	1,437741	33,69	
6	63,2	61,8	53,8	3			U
7	29	30	31	3	1	30	
8							
9	24,5	24,75	27,5	3	1,664582	25,58333	
10							
11	29,3	33,8	29,5	3	2,542309	30,86667	
12							
13							
14	43,5	49,2	0	2	4,030509	46,35	G*
15							
16							
17	37	38	0	2	0,707107	37,5	
18							
19							
20							

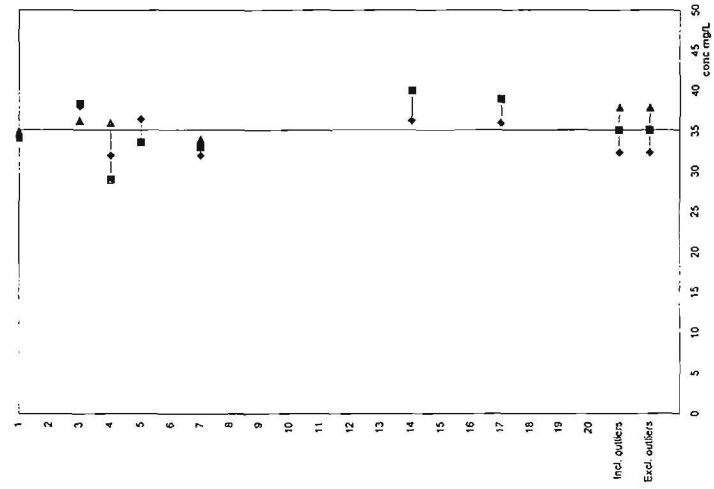
No. of laboratories:	10
No. of laboratories included in the calculations (p):	9
Mean (m):	31,7504
Standard deviation within the laboratories (sr):	2,734842
Standard deviation between the laboratories (sR):	5,959665
Coefficient of laboratories within the laboratories (CVr%):	8,613568
Coefficient of laboratories between the laboratories (CVR%):	18,77036



35-DCP

LAB	1	2	3	n	s(i)	y(i)	Outliers
1	34,4	34,15	34,9	3	0,381881	34,48333	
2							
3	38,07	38,38	36,28	3	1,133593	37,57667	
4	32	29	36	3	3,511885	32,33333	
5	36,48	33,6	33,59	3	1,665663	34,55667	
6							
7	32	33	34	3	1	33	
8							
9							
10							
11							
12							
13							
14	36,3	40	0	2	2,616295	38,15	
15							
16							
17	36	39	0	2	2,12132	37,5	
18							
19							
20							

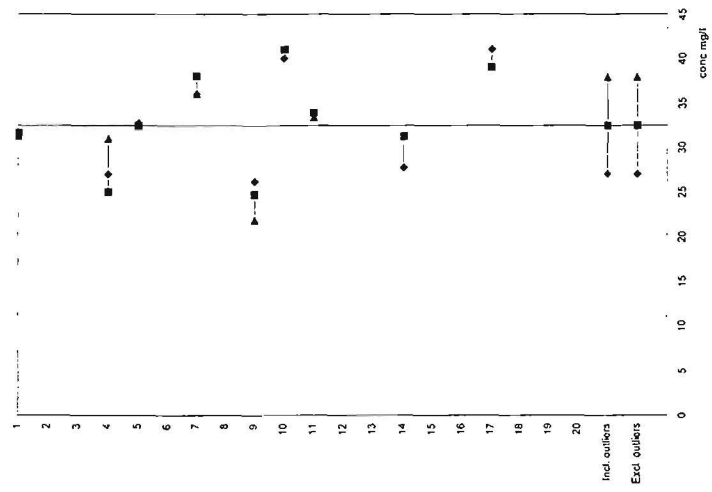
No. of laboratories:	7
No. of laboratories included in the calculations (p):	7
Mean (m):	35,11316
Standard deviation within the laboratories (sr):	1,966856
Standard deviation between the laboratories (sR):	2,790646
Coefficient of laboratories within the laboratories (CVr%):	5,601478
Coefficient of laboratories between the laboratories (CVR%):	7,947579



234-TCP

LAB	1	2	3	n	s(i)	y(i)	Outliers
1	31,7	31,6	31,3	3	0,208167	31,53333	
2							
3							
4	27	25	31	3	3,05505	27,66667	
5	32,74	32,41	32,7	3	0,180093	32,61667	
6							
7	36	38	36	3	1,154701	36,66667	
8							
9	26,2	24,7	21,8	3	2,236813	24,23333	
10	40	41		2	0,707107	40,5	
11	33,7	33,9	33,4	3	0,251661	33,66667	
12							
13							
14	27,7	31,2		2	2,474874	29,45	
15							
16							
17	41	39		2	1,414214	40	
18							
19							
20							

No. of laboratories:	9
No. of laboratories included in the calculations (p):	9
Mean (m):	32,46042
Standard deviation within the laboratories (sr):	1,63795
Standard deviation between the laboratories (sR):	5,43939
Coefficient of laboratories within the laboratories (CVr%):	5,045992
Coefficient of laboratories between the laboratories (CVR%):	16,75699

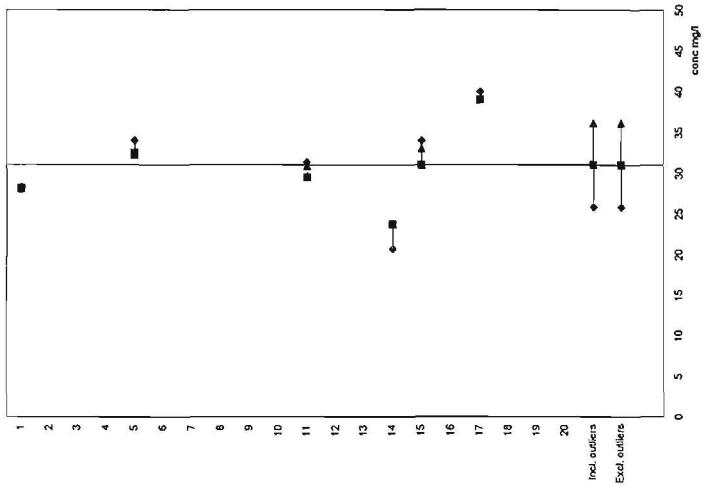


Explanation of outliers

U	Indicates that the laboratory results are not included in the calculation
C*	Indicates Cochran's straggler
G*	Indicates Grubb's straggler
C**	Indicates Cochran's outlier
G**	Indicates Grubb's outlier

235-TCP

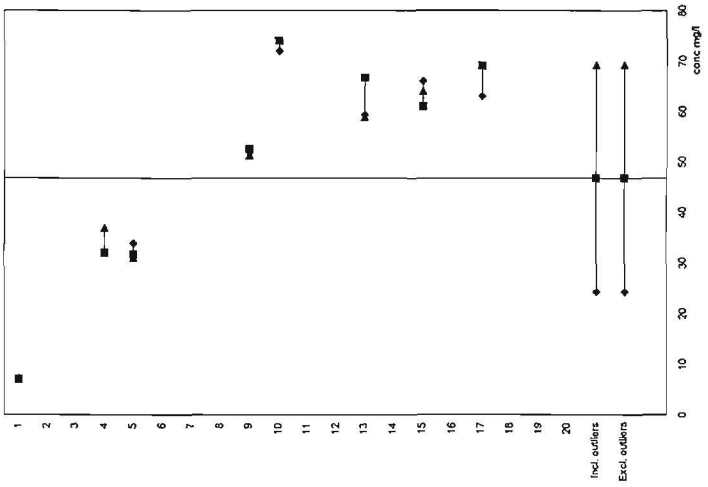
LAB	1	2	3	n	s(i)	y(i)	Outliers
1	28,25	28,15	28,1	3	0,076376	28,16667	
2							
3							
4							
5	34,03	32,5	32,26	3	0,960156	32,93	
6							
7							
8							
9							
10							
11	31,4	29,5	30,9	3	0,984886	30,6	
12							
13							
14	20,7	23,7		2	2,12132	22,2	
15	34	31	33	3	1,527525	32,66667	
16							
17	40	39		2	0,707107	39,5	
18							
19							
20							



No. of laboratories:	6
No. of laboratories included in the calculations (p):	6
Mean (m):	31,03063
Standard deviation within the laboratories (sr):	1,160264
Standard deviation between the laboratories (sR):	5,172807
Coefficient of laboratories within the laboratories (CVr%):	3,739094
Coefficient of laboratories between the laboratories (CVR%):	16,67001

236-TCP

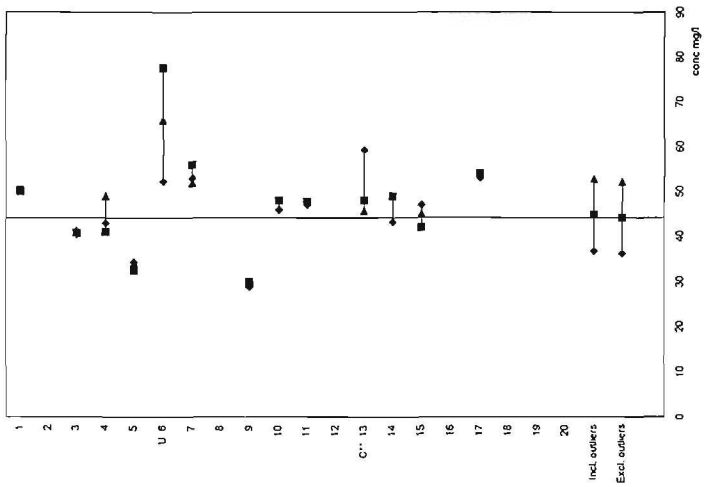
LAB	1	2	3	n	s(i)	y(i)	Outliers
1	7,1	7,05	7	3	0,05	7,05	
2							
3							
4	32	32	37	3	2,886751	33,66667	
5	33,91	31,69	31,09	3	1,48553	32,23	
6							
7							
8							
9	52	52,5	51,3	3	0,602771	51,93333	
10	72	74		2	1,414214	73	
11							
12							
13	59,4	66,7	59	3	4,334743	61,7	
14							
15	66	61	64	3	2,516611	63,66667	
16							
17	63	69		2	4,242641	66	
18							
19							
20							



No. of laboratories:	8
No. of laboratories included in the calculations (p):	8
Mean (m):	46,76
Standard deviation within the laboratories (sr):	2,56
Standard deviation between the laboratories (sR):	22,47
Coefficient of laboratories within the laboratories (CVr%):	5,5
Coefficient of laboratories between the laboratories (CVR%):	48,0

245-TCP

LAB	1	2	3	n	s(i)	y(i)	Outliers
1	50,25	50,25	50,05	3	0,11547	50,18333	
2							
3	40,48	40,79	41,28	3	0,403361	40,85	
4	43	41	49	3	4,163332	44,33333	
5	34,35	32,85	32,58	3	0,953572	33,26	
6	52,3	77,5	65,9	3			U
7	53	56	52	3	2,081666	53,66667	
8							
9	29	29,9	29,5	3	0,450925	29,46667	
10	46	48	0	2	1,414214	47	
11	47,1	47,8	47,8	3	0,404145	47,56667	
12							
13	59,2	48,1	45,7	3	7,202083	51	C**
14	43,2	48,9	0	2	4,030509	46,05	
15	47	42	45	3	2,516611	44,66667	
16							
17	53	54	0	2	0,707107	53,5	
18							
19							
20							



No. of laboratories:	13
No. of laboratories included in the calculations (p):	11
Mean (m):	44,16933
Standard deviation within the laboratories (sr):	2,021581
Standard deviation between the laboratories (sR):	7,9536
Coefficient of laboratories within the laboratories (CVr%):	4,576888
Coefficient of laboratories between the laboratories (CVR%):	18,00706

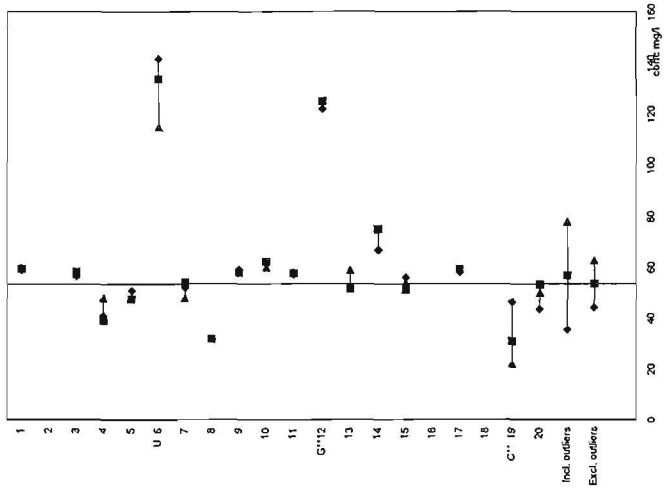
Explanation of outliers

U	Indicates that the laboratory results are not included in the calculation
C*	Indicates Cochran's straggler
G*	Indicates Grubb's straggler
C**	Indicates Cochran's outlier
G**	Indicates Grubb's outlier

246-TCP

LAB	1	2	3	n	s(i)	y(i)	Outliers
1	58,95	59,4	59,65	3	0,35473	59,33333	
2							
3	56,64	58,14	57,3	3	0,751798	57,36	
4	41	39	48	3	4,725816	42,66667	
5	50,87	47,48	47,99	3	1,827868	48,78	
6	141,6	133,6	114,9	3			U
7	52	54	48	3	3,05505	51,33333	
8	32	32	32	3	0	32	
9	59,2	58	58,5	3	0,602771	58,56667	
10	62	62	60	3	1,154701	61,33333	
11	57,2	57,5	58	3	0,404145	57,56667	
12	122	125	125	3	1,732051	124	G**
13	52	51,5	58,9	3	4,135618	54,13333	
14	66,7	74,9		2	5,798276	70,8	
15	56	51	54	3	2,516611	53,66667	
16							
17	58	59		2	0,707107	58,5	
18							
19	46,251	30,77	22,132	3	12,22022	33,051	C**
20	43,5	53	50	3	4,856267	48,83333	

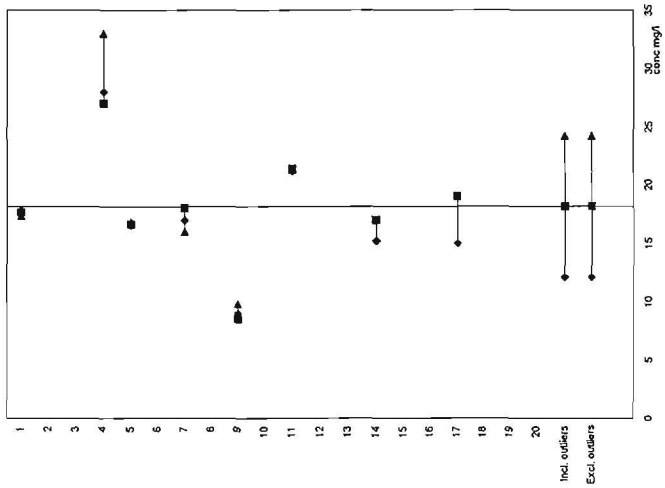
No. of laboratories:	17
No. of laboratories included in the calculations (p):	14
Mean (m):	53,383
Standard deviation within the laboratories (sr):	2,796135
Standard deviation between the laboratories (sR):	9,258666
Coefficient of laboratories within the laboratories (CVr%):	5,237875
Coefficient of laboratories between the laboratories (CVR%):	17,34385



345-TCP

LAB	1	2	3	n	s(i)	y(i)	Outliers
1	17,75	17,65	17,35	3	0,208167	17,58333	
2							
3							
4	28	27	33	3	3,21455	29,33333	
5	16,57	16,62	16,82	3	0,132288	16,67	
6							
7	17	18	16	3	1	17	
8							
9	9	8,5	9,8	3	0,655744	9,1	
10							
11	21,2	21,4	21,3	3	0,1	21,3	
12							
13							
14	15,2	17		2	1,272792	16,1	
15							
16							
17	15	19		2	2,828427	17	
18							
19							
20							

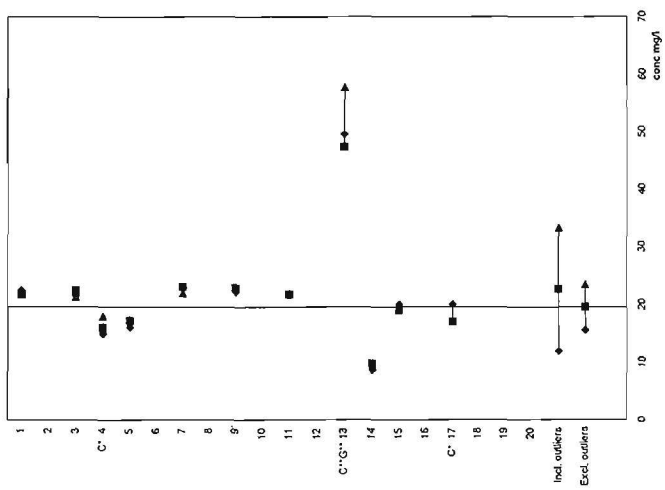
No. of laboratories:	8
No. of laboratories included in the calculations (p):	8
Mean (m):	18,14364
Standard deviation within the laboratories (sr):	1,541992
Standard deviation between the laboratories (sR):	6,050386
Coefficient of laboratories within the laboratories (CVr%):	8,498801
Coefficient of laboratories between the laboratories (CVR%):	33,34715



2345-TeCP

LAB	1	2	3	n	s(i)	y(i)	Outliers
1	22,45	21,75	22	3	0,35473	22,06667	
2							
3	21,58	22,38	21,35	3	0,540648	21,77	
4	15	16	18	3	1,527525	16,33333	C*
5	16,11	17,13	17,39	3	0,67656	16,87667	
6							
7	23	23	22	3	0,57735	22,66667	
8							
9	22,2	22,8	23	3	0,416333	22,66667	
10							
11	21,6	21,7	21,9	3	0,152753	21,73333	
12							
13	49,6	47,3	57,7	3	5,462905	51,53333	C**, G**
14	8,7	9,7	0	2	0,707107	9,2	
15	20	19	20	3	0,57735	19,66667	
16							
17	20	17	0	2	2,12132	18,5	C*
18							
19							
20							

No. of laboratories:	11
No. of laboratories included in the calculations (p):	10
Mean (m):	19,52643
Standard deviation within the laboratories (sr):	0,854565
Standard deviation between the laboratories (sR):	3,923846
Coefficient of laboratories within the laboratories (CVr%):	4,376454
Coefficient of laboratories between the laboratories (CVR%):	20,09505



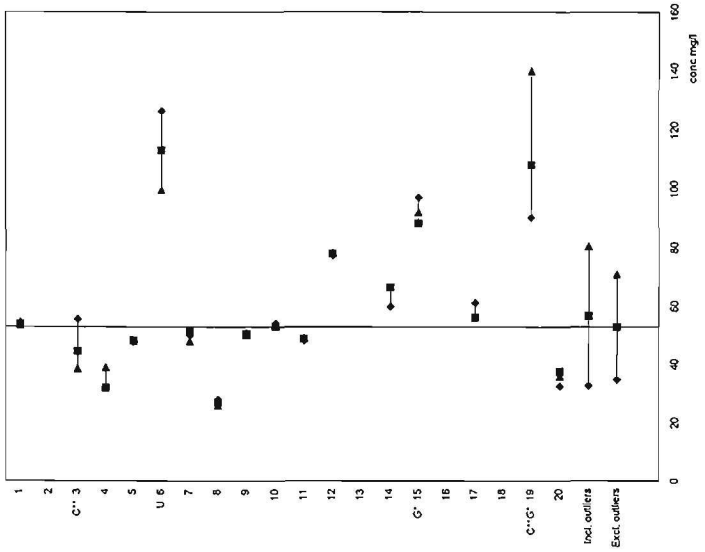
Explanation of outliers

U	Indicates that the laboratory results are not included in the calculation
C*	Indicates Cochran's straggler
G*	Indicates Grubb's straggler
C**	Indicates Cochran's outlier
G**	Indicates Grubb's outlier

2346-TeCP

LAB	1	2	3	n	s(i)	y(i)	Outliers
1	54,3	53,65	53,4	3	0,464579	53,78333	
2							
3	55,43	44,46	38,58	3	8,552171	46,15667	C**
4	32	32	39	3	4,041452	34,33333	
5	47,84	48,2	48,1	3	0,185831	48,04667	
6	126,3	112,9	99,5	3			U
7	50	51	48	3	1,527525	49,66667	
8	28	27	26	3	1	27	
9	50,8	50,5	50,1	3	0,351188	50,46667	
10	54	53	53	3	0,57735	53,33333	
11	48,3	48,5	49	3	0,360555	48,6	
12	77,3	77,8	78,1	3	0,404145	77,73333	
13							
14	59,7	66,2		2	4,596194	62,95	
15	97	88	92	3	4,50925	92,33333	G*
16							
17	61	56		2	3,535534	58,5	
18							
19	90,268	108,135	140,069	3	25,22945	112,824	C**, G*
20	32,5	37,5	36	3	2,565801	35,33333	

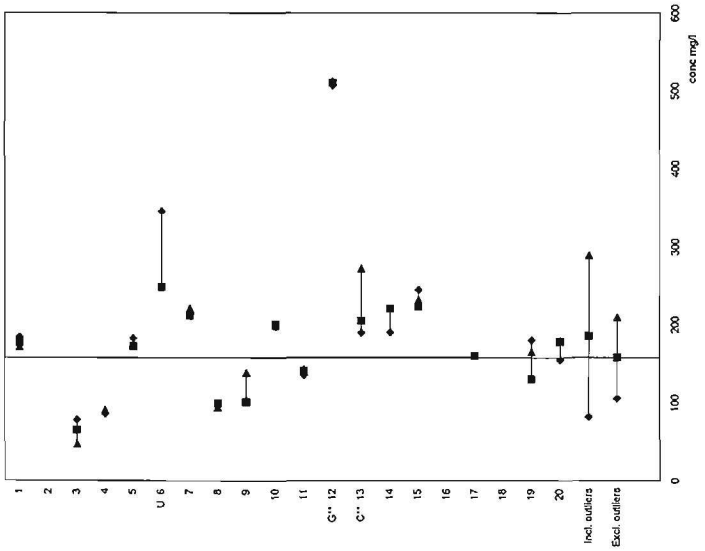
No. of laboratories:	16
No. of laboratories included in the calculations (p):	13
Mean (m):	52,83216
Standard deviation within the laboratories (sr):	2,316538
Standard deviation between the laboratories (sR):	17,99816
Coefficient of laboratories within the laboratories (CVr%):	4,384712
Coefficient of laboratories between the laboratories (CVR%):	34,06667



PCP

LAB	1	2	3	n	s(i)	y(i)	Outliers
1	184	177	172	3	6,027714	177,6667	
2							
3	78,16	64,94	47,31	3	15,47744	63,47	
4	86		91	2	3,535534	88,5	
5	183,09	172,89	174,57	3	5,468894	176,85	
6	345,7	248,5	250,7	3			U
7	216	212	222	3	5,033223	216,6667	
8	100	100	95	3	2,886751	98,33333	
9	103,1	101	139	3	21,35892	114,3667	
10	198	200	199	3	1	199	
11	135,7	140,6	143,2	3	3,808324	139,8333	
12	507	510	512	3	2,516611	509,6667	G**
13	190	205	272	3	43,66158	222,3333	C**
14	190,7	220,6		2	21,14249	205,65	
15	245	223	232	3	11,06044	233,3333	
16							
17	160	160		2	0	160	
18							
19	180,727	130,34	165,726	3	25,87163	158,931	
20	155	178	180	3	13,89244	171	

No. of laboratories:	17
No. of laboratories included in the calculations (p):	14
Mean (m):	157,8629
Standard deviation within the laboratories (sr):	12,72979
Standard deviation between the laboratories (sR):	51,87223
Coefficient of laboratories within the laboratories (CVr%):	8,063826
Coefficient of laboratories between the laboratories (CVR%):	32,85904



Explanation of outliers

U	Indicates that the laboratory results are not included in the calculation
C*	Indicates Cochran's straggler
G*	Indicates Grubb's straggler
C**	Indicates Cochran's outlier
G**	Indicates Grubb's outlier

Appendix 5. Chlorophenol results of all laboratories using own methods

Compound	Sample	N	A	B	C	D	E	F	G	H
23-DCP	A	0			<0.001				<0.01	
	B	0			<0.001				<0.01	
	C	0			<0.005				<0.01	
24-DCP	A	3	0,020		0,031		<0,1		0,020	
	B	3	0,004		0,033		<0,1		0,023	
	C	3	0,986		0,337		<0,1		0,103	
26-DCP	A	2	0,000		0,001				<0,01	
	B	2	0,003		0,001				<0,01	
	C	1	0,064		<0,005				<0,01	
34-DCP	A	2			0,044		<0,1		0,010	
	B	1			0,033		<0,1		<0,01	
	C	2			0,322		<0,1		0,203	
234-TCP	A	1				0,000			<0,01	
	B	1				0,006			<0,01	
	C	2				0,043			0,080	
235-TCP	A	1				0,000			<0,01	
	B	1				0,000			<0,01	
	C	1				0,000			<0,01	
245-TCP	A	3			0,030	0,015	<0,1		0,020	
	B	3			0,028	0,015	<0,1		0,020	
	C	3			0,274	0,157	<0,1		0,350	
246-TCP	A	8	0,275	0,310	0,290	0,257	0,567	0,337	0,147	0,697
	B	6	0,027	0,110	0,092	0,078	<0,1	0,140	0,043	
	C	6	0,971	0,660	1,422	0,752	<0,1	3,340	0,707	
2345-TeCP	A	4	0,022		0,022	0,008			0,013	
	B	2	<0,002		0,044	0,011			<0,01	
	C	4	1,957		0,552	0,422			0,907	
2346-TeCP	A	8	0,997	2,305	2,091	2,047	4,233	2,873	1,333	5,267
	B	8	0,398	1,810	2,240	2,602	4,167	2,363	1,047	3,267
	C	8	83,363	400,000	275,600	200,430	544,800	182,667	294,333	108,000
2356-TeCP	A	1			0,005				<0,01	
	B	0			<0,001				<0,01	
	C	1			<0,005				0,230	
PCP	A	8	1,685	6,155	5,399	6,699	12,867	5,313	4,940	5,233
	B	7	0,083	1,120	1,418	1,445	7,100	1,363	0,580	
	C	7	339		1354	1522	2586	1105	2571	550

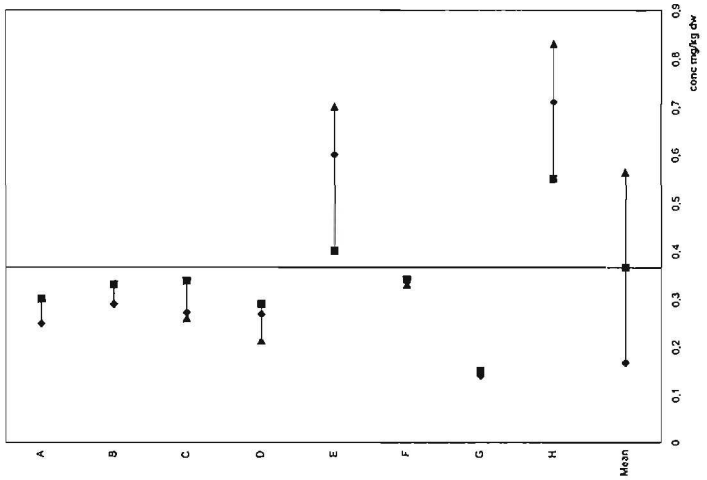
Appendix 6. Line diagrams of chlorophenols analysed from samples A, B and C using own methods

2,4,6-trichlorophenol

Sample A

LAB	1	2	3	n	s(i)	y(i)
A	0,249	0,3		2	0,036062	0,2745
B	0,29	0,33		2	0,028284	0,31
C	0,272	0,338	0,26	3	0,042	0,29
D	0,268	0,289	0,213	3	0,039247	0,256667
E	0,6	0,4	0,7	3	0,152753	0,566667
F	0,34	0,34	0,33	3	0,005774	0,336667
G	0,14	0,15	0,15	3	0,005774	0,146667
H	0,71	0,55	0,83	3	0,140475	0,696667

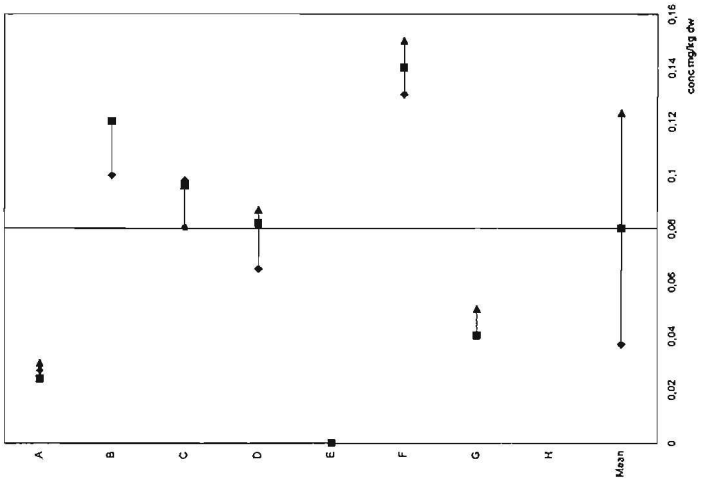
No. of laboratories:	8
No. of laboratories included in the calculations (p):	8
Mean (m):	0,365864
Standard deviation within the laboratories (sr):	0,082365
Standard deviation between the laboratories (sR):	0,198338
Coefficient of laboratories within the laboratories (CVr%):	22,51248
Coefficient of laboratories between the laboratories (CVR%):	54,21085



Sample B

LAB	1	2	3	n	s(i)	y(i)
A	0,0272	0,024	0,03	3	0,003002	0,027067
B	0,1	0,12		2	0,014142	0,11
C	0,098	0,096	0,081	3	0,009292	0,091667
D	0,065	0,082	0,087	3	0,011533	0,078
E	<0.1	<0.1	<0.1	3		
F	0,13	0,14	0,15	3	0,01	0,14
G	0,04	0,04	0,05	3	0,005774	0,043333
H						

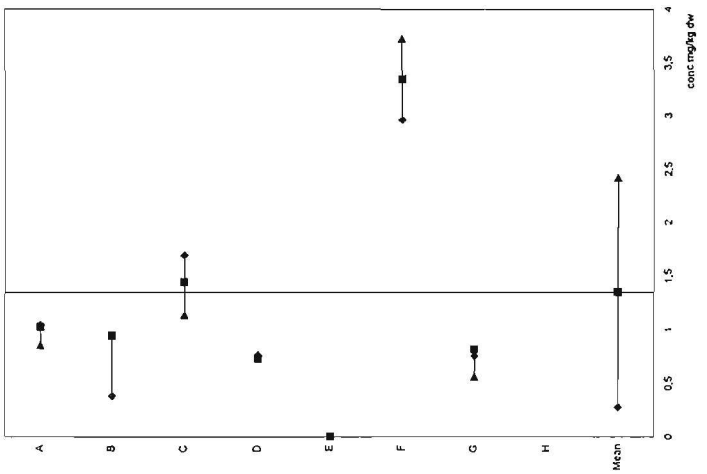
No. of laboratories:	7
No. of laboratories included in the calculations (p):	6
Mean (m):	0,080012
Standard deviation within the laboratories (sr):	0,009162
Standard deviation between the laboratories (sR):	0,0431
Coefficient of laboratories within the laboratories (CVr%):	11,45079
Coefficient of laboratories between the laboratories (CVR%):	53,86682



Sample C

LAB	1	2	3	n	s(i)	y(i)
A	1,04	1,02	0,853	3	0,102679	0,971
B	0,38	0,94		2	0,39598	0,66
C	1,69	1,441	1,136	3	0,277471	1,422333
D	0,76	0,728	0,767	3	0,020793	0,751667
E	<0.1	<0.1	<0.1	3		
F	2,96	3,34	3,72	3	0,38	3,34
G	0,75	0,81	0,56	3	0,130512	0,706667
H						

No. of laboratories:	7
No. of laboratories included in the calculations (p):	6
Mean (m):	1,346765
Standard deviation within the laboratories (sr):	0,244131
Standard deviation between the laboratories (sR):	1,069162
Coefficient of laboratories within the laboratories (CVr%):	18,1272
Coefficient of laboratories between the laboratories (CVR%):	79,38745



Explanation of outliers

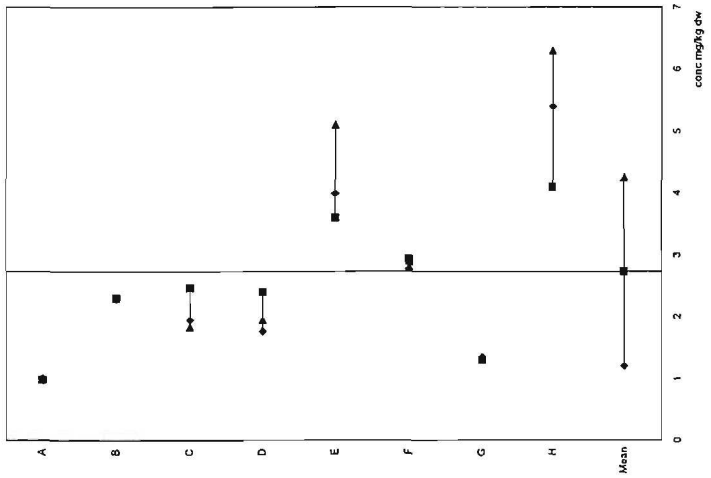
U	Indicates that the laboratory results are not included in the calculation
C*	Indicates Cochran's straggler
G*	Indicates Grubb's straggler
C**	Indicates Cochran's outlier
G**	Indicates Grubb's outlier

2,3,4,6-tetrachlorophenol

Sample A

LAB	1	2	3	n	s(i)	y(i)
A	1,01	0,983		2	0,019092	0,9965
B	2,3	2,31		2	0,007071	2,305
C	1,954	2,471	1,847	3	0,333695	2,090667
D	1,773	2,406	1,963	3	0,324817	2,047333
E	4	3,6	5,1	3	0,776745	4,233333
F	2,78	2,94	2,9	3	0,083267	2,873333
G	1,35	1,3	1,35	3	0,028868	1,333333
H	5,4	4,1	6,3	3	1,106044	5,266667

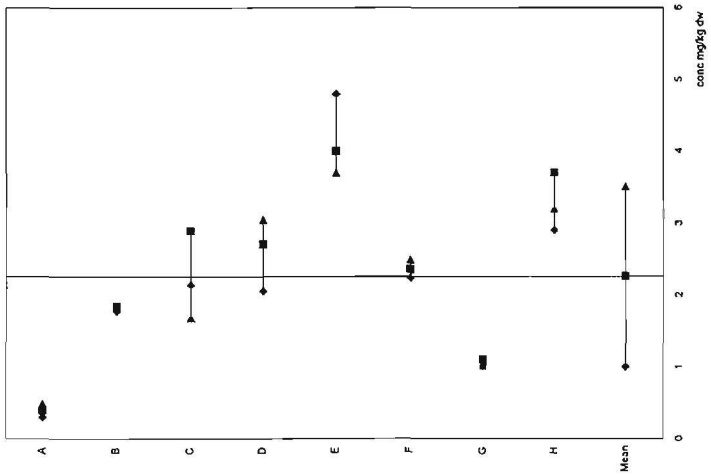
No. of laboratories:	8
No. of laboratories included in the calculations (p):	8
Mean (m):	2,7335
Standard deviation within the laboratories (sr):	0,541361
Standard deviation between the laboratories (sR):	1,524205
Coefficient of laboratories within the laboratories (CVr%):	19,80467
Coefficient of laboratories between the laboratories (CVR%):	55,76021



Sample B

LAB	1	2	3	n	s(i)	y(i)
A	0,307	0,396	0,491	3	0,092016	0,398
B	1,78	1,84		2	0,042426	1,81
C	2,139	2,892	1,688	3	0,60828	2,239667
D	2,056	2,702	3,049	3	0,503947	2,602333
E	4,8	4	3,7	3	0,568624	4,166667
F	2,24	2,36	2,49	3	0,125033	2,363333
G	1,02	1,1	1,02	3	0,046188	1,046667
H	2,9	3,7	3,2	3	0,404145	3,266667

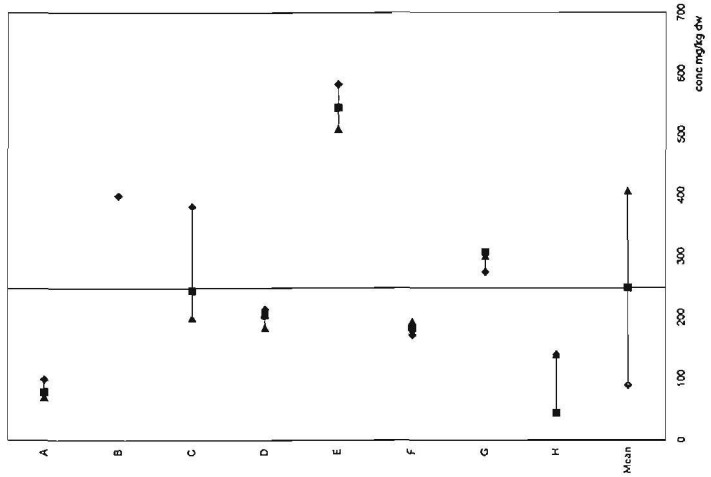
No. of laboratories:	8
No. of laboratories included in the calculations (p):	8
Mean (m):	2,255217
Standard deviation within the laboratories (sr):	0,38949
Standard deviation between the laboratories (sR):	*1,253037*
Coefficient of laboratories within the laboratories (CVr%):	17,27061
Coefficient of laboratories between the laboratories (CVR%):	55,56171



Sample C

LAB	1	2	3	n	s(i)	y(i)
A	99,94	79,07	71,08	3	14,90132	83,36333
B	400			1	0	400
C	382,2	244,3	200,3	3	94,90348	275,6
D	213,71	203,74	183,84	3	15,20761	200,43
E	582,5	543,6	508,3	3	37,11455	544,8
F	172	183	193	3	10,50397	182,6667
G	275	307	301	3	17,0098	294,3333
H	140	44	140	3	55,42563	108

No. of laboratories:	8
No. of laboratories included in the calculations (p):	8
Mean (m):	248,5264
Standard deviation within the laboratories (sr):	45,21243
Standard deviation between the laboratories (sR):	158,6508
Coefficient of laboratories within the laboratories (CVr%):	18,19221
Coefficient of laboratories between the laboratories (CVR%):	63,83662



Explanation of outliers

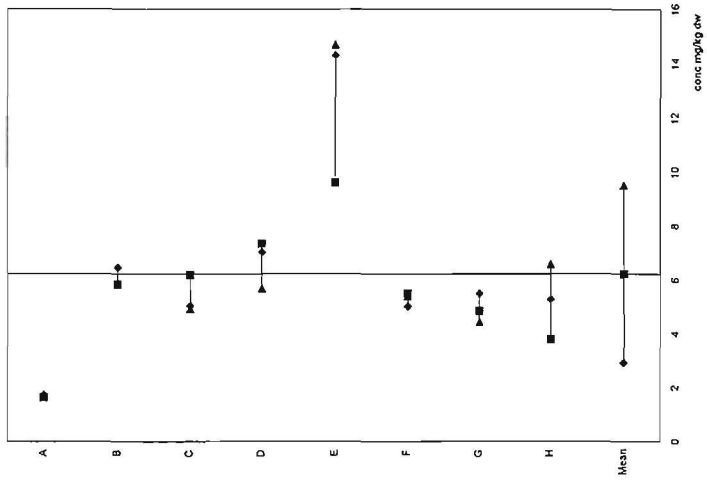
U	Indicates that the laboratory results are not included in the calculation
C*	Indicates Cochran's straggler
G*	Indicates Grubb's straggler
C**	Indicates Cochran's outlier
G**	Indicates Grubb's outlier

Pentachlorophenol

Sample A

LAB	1	2	3	n	s(i)	y(i)
A	1,73	1,64		2	0,06364	1,685
B	6,47	5,84		2	0,445477	6,155
C	5,056	6,189	4,953	3	0,685808	5,399333
D	7,046	7,355	5,696	3	0,882257	6,699
E	14,3	9,6	14,7	3	2,836077	12,86667
F	5,04	5,5	5,4	3	0,241937	5,313333
G	5,51	4,85	4,46	3	0,530754	4,94
H	5,3	3,8	6,6	3	1,40119	5,233333

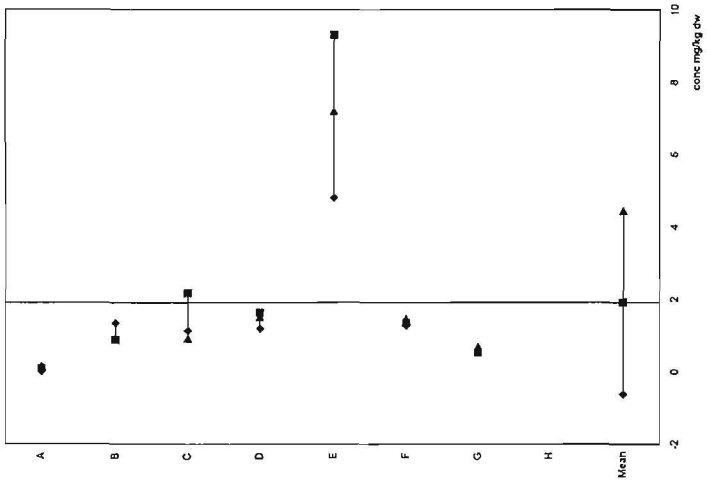
No. of laboratories:	8
No. of laboratories included in the calculations (p):	8
Mean (m):	6,228864
Standard deviation within the laboratories (sr):	1,292664
Standard deviation between the laboratories (sR):	3,285354
Coefficient of laboratories within the laboratories (CVr%):	20,7528
Coefficient of laboratories between the laboratories (CVR%):	52,74404



Sample B

LAB	1	2	3	n	s(i)	y(i)
A	0,0138	0,0943	0,141	3	0,064344	0,083033
B	1,35	0,89	0	2	0,325269	1,12
C	1,143	2,177	0,935	3	0,665205	1,418333
D	1,201	1,62	1,515	3	0,218015	1,445333
E	4,8	9,3	7,2	3	2,251666	7,1
F	1,28	1,35	1,46	3	0,090738	1,363333
G	0,52	0,53	0,69	3	0,095394	0,58
H						

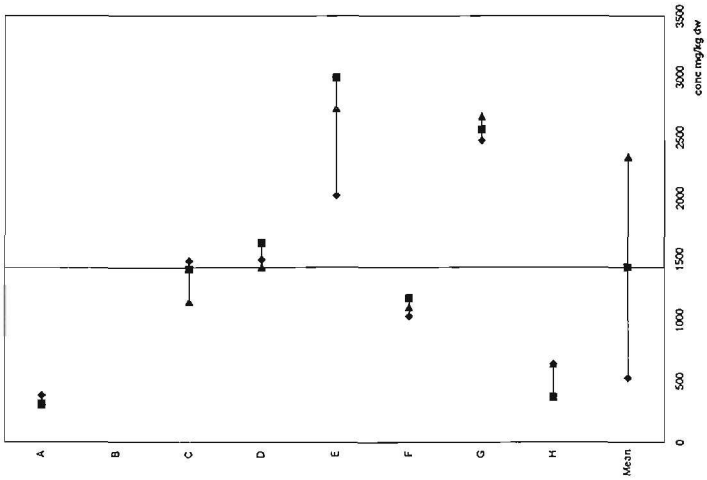
No. of laboratories:	7
No. of laboratories included in the calculations (p):	7
Mean (m):	1,910505
Standard deviation within the laboratories (sr):	0,931038
Standard deviation between the laboratories (sR):	2,527833
Coefficient of laboratories within the laboratories (CVr%):	48,73254
Coefficient of laboratories between the laboratories (CVR%):	132,3123



Sample C

LAB	1	2	3	n	s(i)	y(i)
A	388,5	316,4	311,4	3	43,14282	338,7667
B						
C	1487	1419	1155	3	175,3777	1353,667
D	1497	1631	1437	3	99,32438	1521,667
E	2024,9	2992,4	2741	3	502,0055	2586,1
F	1031	1178	1105	3	73,50057	1104,667
G	2475	2565	2673	3	99,13627	2571
H	640	370	640	3	155,8846	550

No. of laboratories:	7
No. of laboratories included in the calculations (p):	7
Mean (m):	1432,267
Standard deviation within the laboratories (sr):	218,4438
Standard deviation between the laboratories (sR):	905,0363
Coefficient of laboratories within the laboratories (CVr%):	15,25162
Coefficient of laboratories between the laboratories (CVR%):	63,18909



Explanation of outliers

U	Indicates that the laboratory results are not included in the calculation
C*	Indicates Cochran's straggler
G*	Indicates Grubb's straggler
C**	Indicates Cochran's outlier
G**	Indicates Grubb's outlier

Appendix 7. Analysis procedure for chlorophenols in soil

FINNISH ENVIRONMENT INSTITUTE
KIRSTI KALEVI AND KIRSTEN JØRGENSEN
23.12.1996

ANALYSIS PROCEDURE FOR CHLOROPHENOLS IN SOIL

1.1 INTRODUCTION

So far there is no international standard existing for the analysis of chlorophenols in soil samples. The most critical step in chlorophenol analysis from soil samples is the extraction step. The most commonly used methods are based on extraction with organic solvents or with alkaline aqueous solutions.

The method presented here is based on extraction of chlorophenols by acetone-hexane at low pH followed by the acetylation of chlorophenols and analysis of the derivatives by electron capture (EC) gas chromatography.

The presented method has been selected after comparing different commonly used extraction methods in the laboratory and proved it to be the most repeatable and accurate method (Kalevi 1996).

In the inter-laboratory test was used three real soil samples (samples A, B and C) and one standard solution in water (sample D). The real soil samples were obtained from a sawmill site. The soil samples had a natural content of more than 16 different chlorophenol congeners. Sample D was prepared in water from stock solutions of 16 different chlorophenol congeners.

The repeatability variation coefficient, CV_r, which tells about the within-laboratory variation was also satisfactory. It was lower than 8.1% for the test solution and less than 17% for all the soil samples. The results of the inter-laboratory test showed, however, that the reproduciblity between the laboratories to analyze the chlorophenol solution was very poor. The coefficient of variation, CV_R, for the solution ranged from 17.3% to 34.1% and for the soil samples from 31.8% to 71.1%. The variation may be due to the fact that the laboratories used the tested method for the first time and thus had problems to find the right level of concentration.

1.2 SAMPLING

Since chlorophenols are soluble they may leach to deeper layers with the rain water and they may spread with the groundwater. Therefore it is important to know the flow direction of groundwater when planning the sampling program. It is recommended to sample both horizontally and vertically

without mixing the different layers. If the sampling is for a follow-up on a treatment process, e.g. biotreatment, the sampling can be done as combination samples from each treatment bed or pile.

Samples should be sieved through an 8-10 mm sieve. It is convenient to do the sieving in the field if the weather allows it. Samples should be taken in one liter glass vessels with teflon caps, if that much soil is available. It is recommended to fill the vessel completely leaving no air space. The glass vessels must be clean and rinsed with solvent if they are reused. Do not use any kind of plastic containers, since the chlorophenols may adsorb to these.

Warning: When sampling for chlorophenols, skin contact should be avoided. Use gloves and protective clothing. If large amounts of aerosols and dust particles are produced during the sampling, breathing protection may be necessary.

Soil contaminated with commercial mixtures of chlorophenols often contains impurities of polychlorinated phenoxyphenols (PCPPs), polychlorinated dibenzo-p-dioxins and dibenzofurans, and polychlorinated biphenyls (PCBs) in minor concentrations.

1.3 STORAGE OF SAMPLES

Samples should be stored in the dark in the laboratory either frozen or at +4°C. Chlorophenols may be subject to microbial conversion under certain conditions. The ISO standard draft for pretreatment of samples for the determination of organic contaminants proposes maximum 10 days storage time at 4 °C. We do, however, recommend that samples are frozen if they are stored for more than 2 days. This is especially important if the samples are from a biotreatment.

1.4 PRETREATMENT

Homogenization:
Mix the sample in the vessel before taking the subsample. It would be best to analyze the whole amount of sample at one time but it is rarely possible.

Sieving:
Through an 8 mm sieve if the sieving has not been done in the field. The weight of the discarded material should be recorded.

Drying:
Drying is not recommended because practice has shown that both freeze-drying and air drying will diminish recoveries.

1.5 PREPARATION FOR ANALYSIS

This method is modified from Tschochner et al. (1989). This method has proven to be the most repeatable and reproducible when comparing different extraction methods (Kalevi, 1996).

EXTRACTION PROCEDURE:

5 - 20 g (mostly 10 g, sample may be diminished if the concentrations are very high) of natural moist soil + internal standard (ISTD) 2,4,6-tribromophenol (TBrP) are extracted with a mixture of 75 ml of acetone/hexane (1:1) and 1 ml of concentrated HCl. The extract is sonicated for 2 min every 10 min during an hour. The mixture is let to settle and the clear part of the solution is then transferred to a separation funnel and extracted twice with 40 ml of 0.1M NaOH. The combined NaOH-extract is acidified with concentrated HCl (pH must be under 3) and extracted twice with 50 ml of hexane. The hexane solution is then extracted twice with 35 ml of 0.1M K_2CO_3. The chlorophenols in the combined alkaline extract are acetylated as follows: 1 ml of acetic anhydride is added to the carbonate solution and the mixture is shaken vigorously for two minutes to release any carbon dioxide formed in the funnel. The mixture is let to stand for 10 min while shaking occasionally and then 5 ml of hexane is added. The funnel is shaken and the two phases are let to separate. As large portion as possible of the hexane phase is transferred to a vial with 1 g of Na_2SO_4 for drying. After shaking, the hexane solution is transferred to another vial and can be stored with Na_2SO_4 at 4 °C. Analysis of chlorophenols should preferably be done as soon as possible since the chlorophenol acetates are labile towards hydrolysis.

1.6 INSTRUMENTAL METHOD

Equipment:

GC/ECD dual column system for one injection or GC-MS. The use of the equipment must be validated properly.

Temperature program:

80°C, 1,5min --(20°C/min)--> 140°C --(2°C/min)--> 210°C --(20°C/min)--> 270°C, 5min.

Standards:

Commercially available chlorophenol standards for the congeneers to be analyzed and 2,4,6-TBrP as internal standard. In sawmill soil investigations where the Finnish wood preservative KY5 has been used it is recommended to analyze at least 2,4,6-trichlorophenol (246-TCP), 2,3,4,6-tetrachlorophenol (2346-TeCP) and pentachlorophenol (PCP). Standards can be purchased for example from Ehrensdorfer (Germany) and Ultra Scientific (USA).

Calibration:

Calibration is based on peak height and on the response of internal standard (ISTD). Calibration should be done at a suitable concentration level. Several calibrations with different concentration levels are recommended. The amount of ISTD should be as near the amount of the analyzed compounds as possible. Difference of more than one order of magnitude is affecting the results.

This method use an internal standard (ISTD), but other extraction methods may alter the behaviour of the ISTD. This can be eliminated by using an external standard (ESTD). When using ESTD, the exact volume of the analyzed liquid must be known. Also isotope labeled standards can be used.

In this method, two columns are used to ensure the identification of the right components. Because of different polarity of the columns, the same component give different retention times, and can therefore be identified with greater confidence. Separate calibrations are made for each of the two columns.

When the two-column system is used, the average of concentrations obtained from both columns is calculated. If the responses differ, e.g. due to simultaneous elution of impurities in soil samples, the concentration should be based on the smaller response.

The extraction series should always include a zero and a standard sample. It is recommended to do two parallel extractions from the same sample vessel.

1.7 REQUIREMENTS

The method should be validated in each laboratory. The main problem is that no certified reference material at the moment is available on the market. An example of validation results obtained the laboratory of the Finnish Environment Institute is given in the appendix for real soil samples.

For low concentrations the standard variation was found to be around 10% or less. For higher concentrations it was found to vary between 10% and 20%. For 2346-TeCP it was more than 50%. These high deviations were probably due to the heterogeneity of the samples that were obtained from a sawmill site. However, real samples from saw mill sites often contains sawdust and other small pieces of wood, which contain high concentrations of chlorophenols. These would not be included if smaller mesh size was used for sieving and crushing may cause evaporation of the chlorophenols.

The recovery of spiked samples was close to 100%. However, the real recovery of extraction "old" chlorophenols will never be known since the degree of biding may change with time.

The limit values for 2346-TeCP and PCP suggested by the Finnish authorities in 1995 is more than 2 times lower than for the other chlorophenol congeners, since they are the most toxic ones. The detection limits found by the laboratory of the Finnish Environment Institute were below the set guideline limit values.

1.8 TEST REPORT

The results should be given as average ± standard deviation. The results must be calculated and reported in mg/kg dry weight.

When reporting results it is reasonable to give all analyzed chlorophenol compounds separately as well as the total chlorophenol concentration.

The report should contain a copy of the chromatogram of the analysis so that it can be seen which compounds are analyzed and identified and which other peaks are present.

1.9 REFERENCES

Tschochner, F., Pilz-Mittenburg, W., Benz, T., Brunner, H.,Jäger, W. & Hagenmaier, H., 1989. Determination of chlorophenols in aqueous, solid and gas samples by GC/ECD and GC/MS, Z. Wasser-Abwasser-Forsch., vol 22, p. 267-271.

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ISO/CD 14507. Soil quality - Pretreatments of samples for the determination of organic contaminants. Committee Draft 1994-07-14.

KUVAILULEHTI

Julkaisija
Suomen ympäristökeskus

Julkaisun päivämäärä
Maaliskuu 2000

Tekijä(t) (toimielimestä: nimi, puheenjohtaja, sihteeri)

Kirsti Kalevi

Julkaisun nimi (myös ruotsinkielinen)

Kaksi laboratorioiden välistä vertailua kloorifenolien analysoimiseksi maanäytteistä

Julkaisun laji
Raportti

Toimeksiantaja

Toimielimen asettamispvm

Julkaisun osat

Tiivistelmä

Vuosina 1995 ja 1996 järjestettiin Suomen ympäristökeskuksessa kaksi vertailukoetta kloorifenolien analysoimiseksi maanäytteistä. Ensimmäinen vertailu järjestettiin Suomessa käytössä olevien analyysimenetelmien vertailemiseksi. Kaikkiaan kolmetoista laboratoriota osallistui analysoimalla näytteet omilla menetelmillään. Suhteelliset standardipoikkeamat olivat kolmelle pääkomponentille (246-TCP, 2346-TeCP ja PCP) 75.3%:sta 238.5%:iin ja poikkeamatulosten poiston jälkeen 50.9%:sta 198.5%:iin. Tulosten perusteella mikään menetelmä ei osoittautunut suoranaisesti toista paremmaksi.

Toinen vertailukoe järjestettiin liittyen Nordtestin projektiin "Validation and ringtesting of chemical analyses for contaminated soil". Tämä projekti oli jatkoa projektille, jossa annettiin pohjoismaisia suosituksia maanäytteiden analysointimenetelmiksi. Osallistuvia laboratorioita oli 20 ja jokainen sai kolme autenttista maanäytettä ja yhden liuoksena olevan näytteen jonka kloorifenolipitoisuudet tiedettiin. Laboratorioiden piti analysoida näytteet suositellulla Nordtest-menetelmällä , mutta ne saivat lisäksi suorittaa analysoinnin omalla menetelmällään.
Suhteelliset standardipoikkeamat olivat välillä 12.9% ja 90.2%. Tunnetulla liuoksella vastaavat arvot olivat 7.2%:sta 48.0%:iin.
Vertailtaessa omien menetelmien antamia tuloksia, CV_R = 52.7% - 132.3%, kloorifenolien pääkomponenttien (246-TCP, 2346-TeCP, PCP) osalta suositellun Nordtest-menetelmän tuloksiin, CV_R = 12.9% - 71.1%, huomattiin suositusmenetelmän tulosten olevan parempia.

Asiasanat (avainsanat)
kloorifenolit, analytiikka, maanäyte, saastunut maa

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Two interlaboratory comparisons of analysing chlorophenols in soil samples

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Abstract
In 1995 and 1996 the Finnish Environment Intitute arranged two interlaboratory tests concerning analysis of chlorinated phenols in soil samples. The first test was arranged to compare the results of different methods used for analysing chlorophenols in Finland. Finally thirteen laboratories were participating and they analysed samples using their own methods.
The average relative standard variations for three main components of chlorophenols (246-TCP, 2346-TeCP, PCP) were from 75.3% to 283.5% and after exclusion of outliers from 50.9% to 198.5%. There was no clear correlation between the extraction method used and the result obtained.

The second interlaboratory test was arranged between Nordic laboratories in 1996 as a part of Nordtest project "Validation and ringtesting of chemical analyses for contaminated soil". This project was continued after the project that gave recommendations for chemical analysis methods of contaminated soil samples. Participating laboratories were twenty and all of these laboratories analysed the samples with the proposed Nordtest method and eight laboratories also with their own method. The samples were three actual soil samples and one solution with known amounts of chlorophenols.

The reproducibility variation coefficient (CV_R) for soil samples varied from 12.9% to 90.2%. For the known solution these values were from 7.2% to 48.0%. The CV_R ranged for the three main components (246-TCP, 2346-TeCP, PCP) from 52.7% to 132.3% and for the proposed Nordtest method the same variation was from 12.9% to 71.1%. The reproducibility using the Nordtest method was thus significantly better than when using own methods.

Keywords
chlorophenol/s, analytics, soil samples, contaminated soil

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